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U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP718

Part of Journal of Research of the National Bureau of Standards, Volume 13
October 1934

STANDARDIZATION OF LOVIBOND RED GLASSES IN COMBINATION WITH LOVIBOND 35 YELLOW[1]

By Kasson S. Gibson and Geraldine Walker Haupt

ABSTRACT

Inconsistencies in the grades of Lovibond red glasses have long been a source of annoyance and dispute among oil chemists, who use these glasses in the color grading of vegetable oils. Thousands of such glasses are in use in this country, over 2,300 of them having now been submitted to the Bureau for renumbering. A statistical investigation has been made of the uniformity of grades of the first 1,000 glasses and the results recently published in NBS Research Pap. RP653.

The present paper describes the fundamental standardization of the Bureau's Lovibond red glasses, with which these 2,300 glasses have been compared and in terms of which they have been renumbered. The purpose of the standardization was to derive new numerals for the Bureau glasses, approximately equal in magnitude to the original numerals but free from certain inconsistencies occurring among them. The standardization is based upon spectrophotometric analyses of the glasses when in combination with Lovibond 35 yellow. The new numerals were derived from colorimetric computations based on the spectral transmission data, and they are shown to be on a consistent additive scale. This scale covers a range from yellow to yellowish-red. Tolerances of colorimetric purity and light transmission are considered.

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I. INTRODUCTION

The present paper is one of several[2] that have been published in recent years by members of the Bureau staff dealing with the meas-

[1] Credit for secs. II and III of this paper is due in large part to the late Irwin G. Priest, Chief of the Colorimetry Section 1913–32, under whose direction the Lovibond glass standardization program has been performed. The urgency of other work prevented Mr. Priest from preparing the material of these sections for publication, and in March 1931 he requested the authors to prepare the present paper, but without himself as author.

[2] K. S. Gibson, F. K. Harris, and I. G. Priest, *The Lovibond color system—A spectrophotometric analysis of the Lovibond glasses*, BS Sci. Pap. **22**,1(1927-28);S547. D. B. Judd and G. K. Walker, *A study of 129 Lovibond red glasses with respect to the reliability of their nominal grades*, Oil and Fat Industries **5**,16(1928). I. G. Priest, *Tests of color sense of A.O.C.S. members and data on sensibility to change in Lovibond red*, Oil and Fat Industries **5**,63(1928). D. B. Judd, *Effect of temperature change on the color of red and yellow Lovibond glasses*, BS J.Research **1**,859(1928);RP31. I. G. Priest, D. B. Judd, K. S. Gibson, and G. K. Walker, *Calibration of sixty-five 35-yellow Lovibond glasses*, BS J.Research **2**,793(1929);RP58. G. K. Walker, *Statistical investigation of the uniformity of grades of 1,000 Lovibond red glasses*, BS J.Research **12**,269(1934); RP653.

urement and calibration of Lovibond glasses. It describes primarily the method used in standardizing the Lovibond red glasses belonging to the National Bureau of Standards (those having BS inventory number 9940). Thousands of Lovibond red glasses are in use in this country, over 2,300 of them having been submitted to the Bureau since 1927 for calibration in terms of the Bureau's glasses.[3]

This standardization was carried out at the insistence of those who use such glasses in the grading of vegetable oils.[4] The nature of the standardization was dictated by the following considerations:

1. The glasses of set BS 9940 had previously been accepted as "standard" by the Interstate Cotton Seed Crushers' Association, and by the Society of Cotton Products Analysts (now American Oil Chemists' Society).[5]

2. The set had to be standardized within itself; there was no other standard set with which to compare it.

3. The standardization must be based upon fundamental absolute measurements; it must not be dependent upon the permanence of the glasses or of any other material color "standards."

4. The numbers assigned to the glasses when standardized must be additive [6] within prescribed tolerances.

5. The glasses must be combined with some prescribed yellow glass. Because of the color of vegetable oils, the red [7] glasses are always used in combination with Lovibond yellow glasses,[8] and in decisions of greatest importance in combination with a 35-yellow glass.[9] The standardization described in this paper has been carried out, therefore, with the respective red glasses combined with a 35-yellow glass. The values obtained are doubtless valid for a considerable range of yellow glasses on both sides of 35Y; but the values do not necessarily hold for the red glasses used alone or with a Lovibond yellow glass of small numeral.

II. DERIVATION OF THE PRIEST-GIBSON (N'') SCALE AND UNIT

1. DERIVATION AND TEST OF THE N' NUMERALS

To comply with requirement 3 above, the new numerals assigned the glasses must necessarily be derived from their spectral transmissions. The values of spectral transmission for the glasses,

[3] Results obtained on the first 1,000 glasses have been published in BS Research Pap. RP653.

[4] See prefatory statement in BS Sci. Pap. S547.

[5] Proc. Fourth Annual Meeting, Soc. Cotton Products Analysts, pp. 6 and 12, Chicago, June 21, 1913. See also BS Sci. Pap. S547, p.6.

[6] The additivity condition has been expressed (J.O.S.A. & R.S.I., **16**,116; February 1928) as

$$(\Sigma N)_1=(\Sigma N)_2$$

where $(\Sigma N)_1$ and $(\Sigma N)_2$ are the sums of the scale numerals attached respectively to 2 combinations of glasses such that: (1) They contain equal numbers of glasses (nonselective glass of nearly zero absorption being introduced if needed), and (2) they evoke the same color under like conditions. This is the most general case, color being understood in its threefold meaning of hue, saturation, and brilliance. Standardization of the desired type and precision cannot be obtained, however, unless the brilliance of the color is eliminated from consideration. This has accordingly been done (1) in the standardization of the Bureau's glasses (set BS 9940), by giving no weight to the luminous transmission of the glasses in the assignment of the new (N'') numerals, as is explained later, and (2) in the grading of glasses submitted for calibration, by use of the Martens photometer for comparing the test glass with the standards, the criterion for equality being a chromaticity match (hue and saturation only) and the brightnesses of the 2 parts of the photometric field being independently equated by the observer. (See BS Research Pap. RP653.) In such direct comparisons of glasses, also, the maximum number allowed in either beam is 3. Throughout the present paper the term additivity is to be understood as referring to chromaticity rather than color.

[7] The "red" Lovibond glasses are of nonspectral hue, having spectral transmissions of the "gold-ruby" type, in which the principal absorption occurs in the green. (See BS Sci. Pap. S547, fig. 1.)

[8] See, for example, the *Report of Color Committee of the American Oil Chemists' Society, Year 1932-33*, Oil and Soap, **10**, 114 (June 1933).

[9] Rules governing transactions between members of the National Cottonseed Products Association, Inc. (See article 4, rules 60-65.)

N[10]=1.0, 2.0, 3.0 · · · · · 20.0, were used as published in BS Sci. Pap. S547, p. 25, table 1. To comply with requirement 5 of the previous section, the various spectral transmissions were multiplied wave length by wave length by the spectral transmission of a 35-yellow glass. The particular glass used for this purpose was one submitted under test number 41,960; its spectral transmission has been published.[11]

The combination, 35 yellow with variable red, gives a scale varying from yellow to red. This change of hue may be represented by several parameters, the most suitable of which for standardization purposes has proven to be the ratio of the red to the green trilinear coordinates,[12] r/g.

The trilinear coordinates, r, g, b, were computed for each of the 20 glasses (N=1.0, 2.0 · · · · · · · 20.0) of BS 9940 in combination with 35Y of BS test 41960. Plotting values of r/g against values of N gave the results shown in figure 1. A study of these data indicated that, on the average, they could be represented by a quadratic equation with suitably chosen constants. The equation

$$r/g=a+bN+cN^2$$

was, therefore, assumed, in which a has the value of r/g for the 35Y glass alone ($N=0$). Values of the constants b and c were obtained from a least-squares adjustment of the data. The 3 values are as follows:

$$a=1.0958$$
$$b=0.066865$$
$$c=0.00031897$$

A new series of values for these glasses was obtained by inserting values of r/g in the equation and computing new values for N, which were designated N'. Graphically, N' is, of course, the value read from the curve of figure 1 corresponding to a given value of r/g.

The irregular variations of the N scale for the red glasses of BS 9940 with 35Y, shown by the deviations of the plotted points from the curve in figure 1, have been in the more extreme cases well known for many

[10] Throughout the rest of the paper the symbol N refers to the numerals engraved on the glasses as received from the Lovibond establishment.

[11] BS Sci. pap. S547, table 6, p. 30. Figure 9 of that paper gives spectral transmission curves of the red glasses of BS 9940, N=1.0 to 20.0, in combination with a 35-yellow glass.

[12] The constants used in computing the trilinear coordinates of the Lovibond glasses are as given in table 1, p. 525, of BS Research Pap. RP163. (Deane B. Judd, *Reduction of data on mixture of color stimuli*, BS J.Research (April 1930).) The values of ρ_1, γ_1, and β_1 there given represent the distributions of the "O.S.A. excitations" (extrapolated) throughout the spectrum of Abbot-Priest sunlight. If T represent the spectral transmission of a glass or combination of glasses, r, g, and b are defined and computed as:

$$r=\frac{\Sigma\rho_1 T}{\Sigma\rho_1 T+\Sigma\gamma_1 T+\Sigma\beta_1 T},$$

$$g=\frac{\Sigma\gamma_1 T}{\Sigma\rho_1 T+\Sigma\gamma_1 T+\Sigma\beta_1 T},$$

$$b=\frac{\Sigma\beta_1 T}{\Sigma\rho_1 T+\Sigma\gamma_1 T+\Sigma\beta_1 T},$$

the summations being taken at every 10 mμ from 380 to 720 mμ.

From this it is apparent that $r/g=\frac{\Sigma\rho_1 T}{\Sigma\gamma_1 T}$. The values of b do not enter into the computation of r/g but are used in computing the colorimetric purity, as described later.

years, being thoroughly established by various preliminary calibrations of one sort or another.[13]

The N' scale, derived by the least-squares adjustment just described, represents the average Lovibond red scale (when in combination with 35Y) as established from the numerals engraved on the glasses by the Tintometer, Ltd., insofar as the 20 red glasses of BS 9940 used in its derivation represent the average of all Lovibond red glasses of like denomination in existence. The degree to which these 20 glasses represent the average of all the Lovibond red glasses so far examined is discussed in section VI.

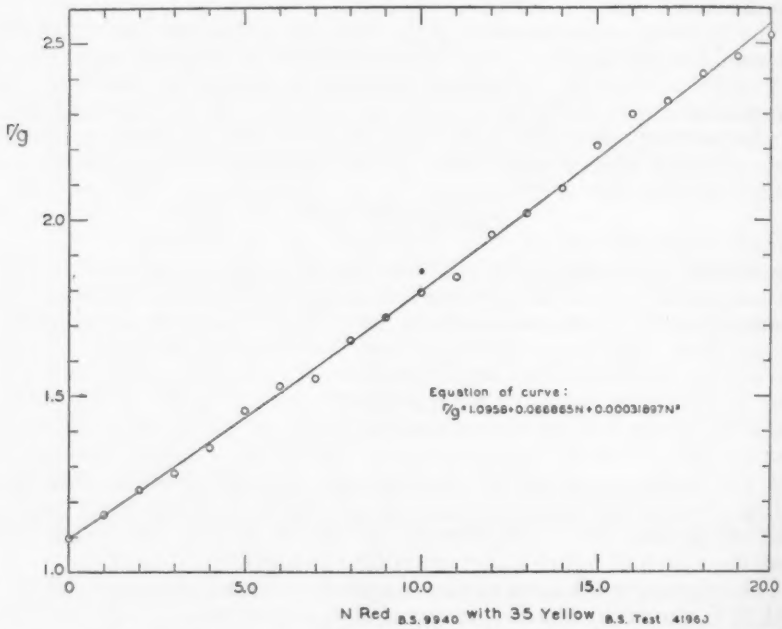

FIGURE 1.—*Relation between r/g and N for Lovibond red glasses (with 35 yellow).*

r/g is the ratio of red to green trilinear coordinates, *N* the Lovibond numeral. Deviations of the circles from the curve illustrate the erratic variations in the scale as found for the Bureau glasses, BS 9940.

To comply with requirement 4 of section I, it was necessary to test the N' numerals with respect to their additivity. For any scale to be additive, it is necessary and sufficient that the unit be constant throughout the scale, so that any given glass should give a constant additional numerical value when combined with any of the various glasses comprising the scale. Such a test of the N' scale was carried out by computation as shown in table 1.

[13] See, for example, BS Sci. Pap. S547, p. 8. In view of the relatively large variations existing among red glasses of the same nominal value, as found during the statistical investigation described in BS Research Pap. RP653, erratic deviations such as are shown in figure 1 are to be expected.

TABLE 1.—*Derivation of N′ unit and additive scale for Lovibond red glasses (BS 9940) combined with 35 yellow (BS test 41960)*

[See text for explanation]

1	2	3	4	5	6	7	8	9	10	11	12
N	N'_N	$N'_{N\&1}$	$N'_{N\&1}-N'_N \equiv (\Delta N')_{N\&1}$	$(r/g)_N$	$(r/g)_{N+1}$	$(r/g)_{N\&1}$	$(r/g)_{N+1}-(r/g)_N \equiv \Delta(r/g)_{N+1}$	$(r/g)_{N\&1}-(r/g)_N \equiv \Delta(r/g)_{N\&1}$	$\frac{\Delta(r/g)_{N+1}}{\Delta(r/g)_{N\&1}}$	$1.173\frac{\Delta(r/g)_{N+1}}{\Delta(r/g)_{N\&1}} \equiv (\Delta N')_{N+1}$	$N'_N \equiv N'_{r/g}$
1.0	1.01	2.08	1.07	1.1640	1.2338	1.2370	0.0698	0.0730	0.9562	1.122	1.173
2.0	2.04	3.15	1.11	1.2338	1.2805	1.3097	.0467	.0759	.6153	.722	2.295
3.0	2.73	3.87	1.14	1.2805	1.3541	1.3592	.0736	.0787	.9352	1.097	3.017
4.0	3.80	4.97	1.17	1.3541	1.4572	1.4366	.1031	.0825	1.2497	1.466	4.114
5.0	5.27	6.48	1.21	1.4572	1.5270	1.5433	.0698	.0861	.8107	.951	5.580
6.0	6.26	7.49	1.23	1.5270	1.5495	1.6144	.0225	.0874	.2574	.302	6.531
7.0	6.58	7.79	1.21	1.5495	1.6561	1.6363	.1066	.0868	1.2281	1.441	6.833
8.0	8.07	9.29	1.22	1.6561	1.7232	1.7438	.0671	.0877	.7651	.897	8.274
9.0	9.00	10.24	1.24	1.7232	1.7926	1.8142	.0694	.0910	.7626	.895	9.171
10.0	9.95	11.18	1.23	1.7926	1.8363	1.8829	.0437	.0903	.4839	.568	10.066
11.0	10.54	11.78	1.24	1.8363	1.9554	1.9274	.1191	.0911	1.3074	1.534	10.634
12.0	12.15	13.34	1.19	1.9554	2.0172	2.0443	.0618	.0889	.6952	.815	12.168
13.0	12.98	14.17	1.19	2.0172	2.0873	2.1067	.0701	.0895	.7832	.919	12.983
14.0	13.91	15.09	1.18	2.0873	2.2080	2.1774	.1207	.0901	1.3396	1.571	13.902
15.0	15.49	16.65	1.16	2.2080	2.2980	2.2976	.0900	.0896	1.0045	1.178	15.473
16.0	16.66	17.81	1.15	2.2980	2.3341	2.3873	.0361	.0893	.4043	.474	16.651
17.0	17.12	18.27	1.15	2.3341	2.4119	2.4234	.0778	.0893	.8712	1.022	17.125
18.0	18.12	19.24	1.12	2.4119	2.4622	2.5004	.0503	.0885	.5684	.667	18.147
19.0	18.76	19.84	1.08	2.4622	2.5248	2.5480	.0626	.0858	.7296	.856	18.814
20.0	19.55	------	------	2.5248	------	2.6101	------	.0853	------	------	19.670
Mean (column 4)------			1.173	------	------	------	------	------	------	------	------

Values of N'_N (column 2) are those obtained from the least-squares solution of the $(r/g, N)$ curve noted above. The r/g values for the respective glasses are tabulated in column 5, labelled $(r/g)_N$.

Columns 7 and 3 were derived as follows: The spectral transmissions of the respective glasses from 1 to 20, in combination with the 35Y glass, were each in turn multiplied by the spectral transmission of the nominal unit glass ($N=1.0$) and the r, g, and b values for the respective combinations computed in the same manner as for the individual glasses. That is, the values of column 7 were derived from the respective spectral-transmission products, 35Y×1R×1R, 35Y×2R×1R, 35Y×3R×1R, etc., just as the values of column 5 had been derived from the similar products 35Y×1R, 35Y×2R, 35Y×3R, etc. The N' values of column 3, designated as $N'_{N\&1}$, were derived from the r/g values of column 7 by reading from the least-squares curve illustrated in figure 1.

The variable nature of the N' scale is shown by the values of $\Delta N'_{N\&1}$ of column 4. It is seen that the nominal unit glass ($N=1.0$), when combined with the other glasses, has an effective value varying from 1.07 to 1.24, although the value obtained for the glass by itself (column 2) is only 1.01. The average value of this glass is approximately 1.17 instead of unity.

This variation of the unit throughout the scale, in addition to the erratic variations illustrated in figure 1, shows clearly the need and importance of the regrading of Lovibond red glasses when they are

to be used with 35Y or any other Lovibond yellow glass of high numeral. The adjustments required to establish a new (N'') scale, insuring compliance with the additivity condition, will now be described.

2. DERIVATION OF THE N'' UNIT AND NUMERALS

It has just been shown that the N' scale is a smooth one but that since $\Delta N'_{N\&1}$ is not constant, this scale does not satisfy the additivity condition. To make the new (N'') scale satisfy this condition it must be such that $\Delta N''_{N\&1}$ is a constant; and since it is important to have numbers on the N'' scale nearly equal to numbers for the same glasses on the N' scale, this constant was taken at 1.173, the average value of $\Delta N'_{N\&1}$ (see column 4). Assignment of N'' values to the glasses of the red series was then carried out according to the formula

$$N''_{N+1}=N''_{N}+1.173\frac{\Delta N'_{N+1}}{\Delta N'_{N\&1}}, \tag{1}$$

which defines the N'' value of any glass, $N+1$, in terms of the glass, N, just below it in the series. The further natural condition was added that $N''_{N}=0$ for 35Y alone, or with clear glass.

Equation 1 is derived from the fact that the interval between any 2 glasses, N and $N+1$, must bear a constant ratio to the interval represented by the nominal unit glass, $N=1$, regardless of the scale on which these intervals are expressed. Therefore,

$$\frac{\Delta N''_{N+1}}{\Delta N''_{N\&1}}=\frac{\Delta N'_{N+1}}{\Delta N'_{N\&1}}$$

The additivity of the N'' scale is automatically insured by giving $\Delta N''_{N\&1}$ a constant value, as stated above. If this value be taken at 1.173 and $\Delta N''_{N+1}$ be expressed as $N''_{N+1}-N''_{N}$, equation 1 follows.

In the actual computation of the N'' values for the 20 red glasses the following nearly equivalent formula was used:

$$N''_{N+1}=N''_{N}+1.173\,\frac{\Delta(r/g)_{N+1}}{\Delta(r/g)_{N\&1}} \tag{2}$$

which substitutes r/g steps for N' steps in formula 1. The 2 formulas would be identical if r/g were linearly connected to N'; the relatively small coefficient of the N^2 term (see fig. 1) suggests that the 2 formulas are not significantly different, and tests by actual computation substantiate this.

The values of N''_{N} in column 12, table 1, are obtained according to equation 2, the values of the last term of this equation being given in column 11. Note, for example, that for $N=0$ equation 2 gives $1.173=0+1.173$; for $N=1$, $2.295=1.173+1.122$; and so on. These values of N''_{N} in view of their method of derivation will be hereafter referred to as $N''_{r/g}$, as will be other values obtained specifically by way of spectral transmission and r/g computation. However, the subscript r/g will be omitted where the emphasis is primarily upon the N'' value rather than the mode of determination.

The values of $N''_{r/g}$ thus obtained for the 20 glasses of set BS 9940 having values of $N=1.0, 2.0, 3.0, \cdots\cdots 20.0$ were used to plot a

standard curve from which the value of $N''_{r/g}$ for any other glass might be obtained after its spectral transmission had been determined. This curve is illustrated in the lower part of figure 2.

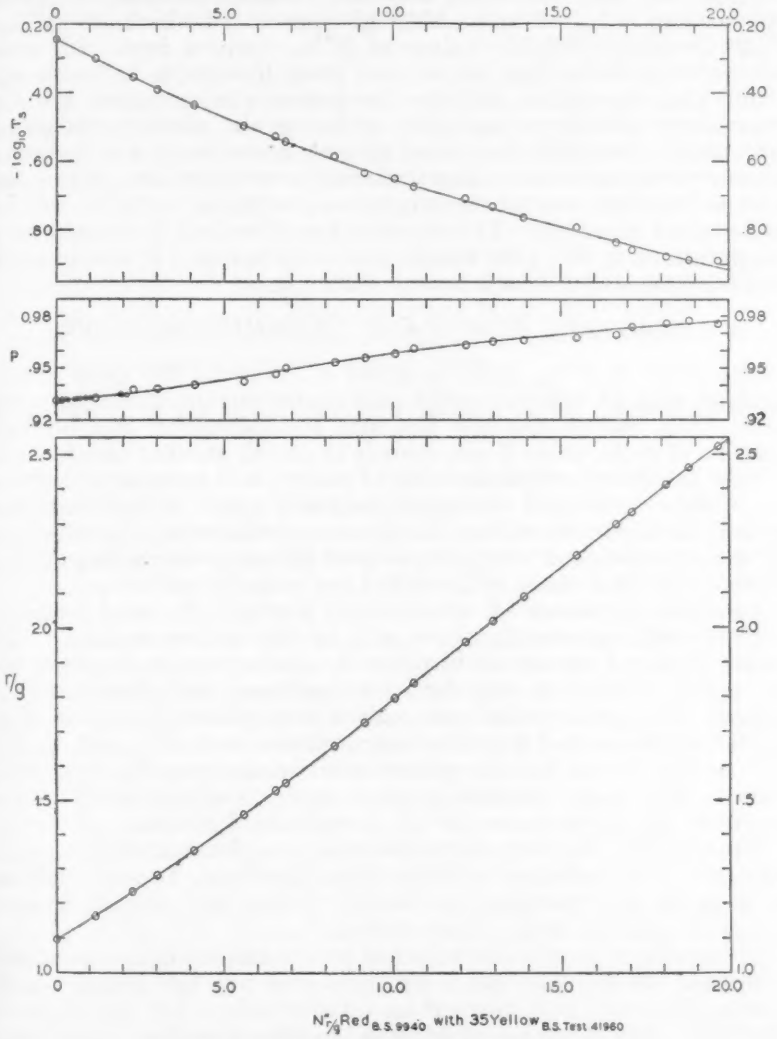

FIGURE 2.—*Standard curves on the N'' scale.*

The lower curve compared with figure 1 shows the elimination of the erratic variations in the values assigned to the glasses of BS 9940 in the present standardization. The middle and upper curves show respectively the values of colorimetric purity, P, and sunlight transmission, T_s (on a log scale), plotted as functions of $N''_{r/g}$.

Computation of N'' for glasses having values of N equal to 1.0 or less. The curve just illustrated, r/g vs $N''_{r/g}$, was not, however, wholly suitable for obtaining values of $N''_{r/g}$ for values of N less than 1.0.[14]

[14] The spectral transmissions of the glasses, N=0.01, 0.02, 0.03, ····· 0.09, 0.10, 0.20, 0.30 ····· 0.90, of BS 9940, were measured in 1926–27, but have not been published.

On the scale shown, values could not be read with the desired precision, and any attempt at magnification would have been rather unsatisfactory because of the slight curvature of the line in this region. A straight line was, therefore, assumed to hold between the points representing $N''_{r/g}=0$ and 1.173, the equation of which is[15] $N''_{r/g}=17.22215\ (r/g-1.09587)$. Values of $N''_{r/g}$ derived from this equation did not differ from those read from the graph by more than 0.01. This agreement justifies the use of the equation, since an uncertainty of 0.01 is negligible so far as the absolute values are concerned. For these fractional glasses, however, it was desired to determine values with a computational uncertainty not greater than 0.001 so that differences between glasses nearly alike could be obtained with greater precision. The equation has, therefore, been used for all computations of $N''_{r/g}$ for values of $N=1.0$ or less. It should not be used for values of N much greater than 1.0.

3. STANDARD PURITY AND TRANSMISSION CURVES

The value of $N''_{r/g}$ to be assigned a Lovibond red glass in combination with 35 yellow is valid only under certain additional conditions. Not merely the hue but also the saturation and brilliance must be of given value if one color is to match another satisfactorily. For the Lovibond red glasses with 35 yellow, it is necessary, therefore, to consider standard colorimetric-purity and light-transmission curves and corresponding tolerances. Otherwise, "grades" via r/g could be assigned a large variety of glasses giving colors differing enormously from those of Lovibond red with 35 yellow.

Accordingly, values of colorimetric purity,[16] P, were computed from the trilinear coordinates (r,g,b), by the routine method.[17] The values obtained are shown in figure 2, middle section, together with the curve adopted as standard for Lovibond red glasses with 35 yellow. It may be noted that values were plotted for some of the fractional glasses and for a few extra glasses near $N''_{r/g}=2$, in addition to the values for the glasses used in deriving the $(r/g, N''_{r/g})$ curve. This made possible a more accurate estimate of the true course of the purity curve for the lower-valued glasses.

The standard light-transmission curve was determined in a similar manner. Transmissions for Abbot-Priest sunlight, T_s, were computed by a previously described method.[18] Values of $-\log_{10}T_s$ thus obtained are plotted in fig. 2, top section.[19]

In general, of course, the values of purity and sunlight transmission computed for any Lovibond red glass will not fall exactly on the standard curves, any more than do the values for the glasses of BS 9940. The question of permissible tolerances has, therefore, to be considered. The purity deviations and tolerances may be expressed as $P-P_{N''}$, where P is the actual purity of the glass as defined above and $P_{N''}$ is the purity as read from the standard curve at the value of $N''_{r/g}$ found for the glass. In figure 2 this difference

[15] A slight inconsistency may be noted between the value of r/g here given for 35Y (=1.09587) and that given previously (a=1.0958), which is due to rejection errors. The use of 1.0958 in the present equation would not change any of the values of $N''_{r/g}$ by more than 0.001.

[16] Irwin G. Priest, *The computation of colorimetric purity*, J.O.S.A. & R.S.I., **9**, 503(1924).

[17] Deane B. Judd, *The computation of colorimetric purity*, J.O.S.A. & R.S.I., **13**, 143(1926).

[18] BS Sci. Pap. S547, p. 17.

[19] The value for $N''_{r/g}=0$ was determined as follows: T_s for $35Y_{BS\ test\ 41,040}$ (alone) equals 0.6319. The value of T_s for a zero glass was taken as 0.901, which is the mean of the values given for T_s for the zero red, yellow, and blue glasses (BS Sci. Pap. S547, tables 1, 2, and 3). $0.6319\times0.901=0.5693$; and $-\log_{10}0.5693=0.2447$, which is the value of the intercept as plotted.

is represented by the vertical distances between the plotted points and the standard purity curve. The magnitude of these deviations is further illustrated and discussed in section IV, where the question of tolerances is considered.

Deviations of the actual sunlight transmissions (or $-\log_{10}T_s$ values) from the values proper to $N''_{r/g}$ could be similarly expressed, and are likewise illustrated in figure 2 by the vertical distances between the plotted values and the standard $-\log_{10}T_s$ curve. As explained in footnote 6, p. 434, however, the additivity condition refers to chromaticity alone, and in the determination of N'' the sunlight transmission is eliminated as a determining factor. Such data would be of no use under the present customary conditions of using the glasses to grade oils. It is, of course, true that there must be limits of such transmission, even though wide, outside of which a glass would be unusable in the oil trade. The value of such limits is not known, however, and since no glass has been found objectionable in this respect, the question of luminous transmissions of the glasses will not be further considered in the present paper.

4. SELECTION OF STANDARDS FOR ROUTINE CALIBRATION OF LOVIBOND RED GLASSES

The purpose of the Bureau's standardization was not merely the establishment of an accurate additive scale but also the selection of a certain number of glasses so distributed in N'' value that glasses submitted for test could be directly compared with them and graded. While the calibration of any Lovibond red glass with 35 yellow can be carried out via spectral transmission measurement and computation, as illustrated in the previous section, this would be a much too laborious and costly procedure for calibrating the thousands of Lovibond red glasses used in the vegetable oil industry. With standardized glasses available, the time required for the calibration of a glass by the direct-comparison method is but a small fraction of that necessary by the spectrophotometric method.

The obvious choice of glasses to serve as comparison standards would be those whose values of N'' equal, respectively, 0.10, 0.20, ... 0.90, 1.0, 2.0, ... 10.0, 20.0; that is, a decimal system, so that any test glass could be matched by a combination of not more than 2 (or 3, above 10.0) glasses.[20] Accordingly, most of the red glasses of BS 9940 which had not already been standardized [21] were compared with combinations of the standardized glasses giving as nearly as possible the desired values of exact tenths and units on the N'' scale.[22] Four observers [23] took part in this study, the observations being made with a Martens photometer having a 35Y glass over the ocular and with illumination produced by natural north skylight through milk glass.[24] Those glasses nearest matching the selected

[20] Since the Lovibond red glass of smallest nominal value (N=0.01) has an N'' value of approximately 0.1, it is not feasible to extend the decimal system to glasses having values of N'' less than 0.1. Furthermore, the change in chromaticity caused by a glass of N''=0.1 (when combined with 35 yellow, N red) is so small that further subdivision would be an unnecessary refinement, even if possible.

[21] That is, all the glasses excepting those having values of N=0.01, 0.02, ... 0.09, 0.10, 0.20, ... 0.90, 1.0, 2.0, ... 10.0. This comparison did not include glasses with values of N greater than 10.0.

[22] It was possible by combining not more than 3 of the standardized glasses to secure combinations having values of N'' differing from the desired exact tenths and units by not more than ±0.006 over the range from N''=0.1 to N''=10.0.

[23] Deane B. Judd, J. O. Riley, and the authors made these observations under the supervision and direction of Mr. Priest.

[24] This apparatus is illustrated in Oil and Fat Industries, **5**, 17 (January 1928).

combinations were then measured spectrophotometrically and the values of $N''_{r/g}$ computed.[25] Other glasses from BS 9940 were later measured until to date a total of 78 red glasses from BS 9940 have undergone spectrophotometric standardization. Those selected as working standards for the regrading of glasses submitted for calibration are listed in BS Research Pap. RP653, p.271.

III. EXPERIMENTAL TESTS OF ADDITIVITY OF THE N'' SCALE

The values of N' and N'', and therefore the scale and unit, established with the glasses of BS 9940 in the present standardization would be essentially unchanged regardless of (1) the particular 35Y glass used in combination with the red glasses, (2) the energy distribution used to represent the source, within certain limits, and (3) the visual characteristics assumed for the hypothetical normal observer—although once the scale is established, the exact values of the various constants used in its derivation must always be used in computing $N''_{r/g}$ for any unknown glass. Reasonable variations of these factors do not, therefore, have any bearing on the relative merits of the N'' and N scales. It should be remembered, however, that all the conclusions stated refer to Lovibond red glasses in combination with 35 yellow. Similar conclusions might perhaps be reached by a study of the red glasses alone (without 35Y) or in combination with other glasses, but such is not demonstrated in the present paper.

The computational superiority of the N'' scale over the N and N' scales has already been demonstrated. There remains, however, the very important question of the practical utility of the N'' scale. This has been satisfactorily answered by means of various tests showing its additive nature. These tests have been gradually accumulated since the scale was inaugurated. A brief résumé of the results of several of these follows.

1. The practicability of the N'' scale was to a considerable degree ascertained at the time the standards were selected. It was found that (1) a given chromaticity could be matched by combinations of glasses having nearly the same value of $N''_{r/g}$ but considerably differing values of N, (2) the N'' values of the single glasses selected to match the combinations were on the average not significantly different (0.04 less) from the N'' values of the combinations.

2. An extensive intercomparison of the standards from 0.1 to 10.0 was later made by D. B. Judd and G. K. Walker with improved illumination.[26] In this investigation, various standards were combined in pairs and a third standard selected which nearly matched the combination. The residual difference was then estimated; or, if such difference was greater than $N'' = 0.1$, a fourth standard approximating the difference was introduced and the residual difference again estimated. The N'' value of the combination of the first 2 glasses was then compared with the N'' value of the third glass plus residual (or plus fourth glass plus residual). The latter exceeded the former on the average by approximately 0.03, this difference being, however, opposite in sign to the average difference found under 1, just above. Individual

[25] The degree of agreement between values of N'' obtained via spectral transmission measurement and computation and values of N'' obtained by direct comparison with standardized glasses, is illustrated in sections IV and V.

[26] Artificial sunlight, apparatus as described in BS Research Paper RP653.

discrepancies rarely exceeded 0.12; the agreement was considered sufficiently satisfactory that a contemplated N''' scale was not formulated.

3. A series of red glasses, $N=0.1, 0.2 \cdots\cdots 0.9, 1.0, 2.0, \cdots\cdots 10.0$, were submitted under BS test 41,960.[27] In the course of this test, it seemed desirable to see if the same values of N'' would be obtained for the fractional glasses when they were combined with 7.0R as when used alone (in both cases in combination with 35Y, as usual). Accordingly, the spectral transmission of each fractional glass was combined with that of 7.0R, 35Y and values of $N''_{r/g}$ computed for the combinations. The values of $N''_{r/g}$ for 7.0R, 35Y alone was then subtracted from the values for the combinations and the resulting differences compared respectively with the values of $N''_{r/g}$ obtained for the fractional glasses alone (with 35Y) obtained in the regular way. The differences in no case exceeded 0.02, indicating that within this tolerance these fractional glasses had the same respective values at these 2 widely differing places on the scale.

4. Most conclusive of all is the evidence afforded by the observations made on the approximately 2,300 red glasses that have been submitted for calibration. In these measurements,[28] the test glass is given a tentative regrade (N'') value by comparison with the standard glasses of BS 9940. After all the glasses submitted at any one time have been thus tentatively graded, they are intercompared. That is, a standard is chosen equal (or closely equivalent) in N'' value to the difference between the tentative values assigned to adjacent test glasses. This is done throughout the whole range of test glasses. If a satisfactory intercheck is not observed, the test glasses involved are reexamined, the cause of the discrepancy located, and new values assigned where necessary, until finally, the whole set of test glasses is consistent within itself and with the standards. This intercheck would prove impossible if the standards themselves were not additive within the desired tolerances. The fact that it has been possible for the many hundreds of test glasses submitted insures the additivity of the standards within the desired tolerances.

IV. COMPARISON OF N'' VALUES OBTAINED VIA SPECTRAL TRANSMISSION AND COMPUTATION OF r/g, AND VIA DIRECT COMPARISON WITH THE STANDARDS

It has been shown in the previous section that the scale established for Lovibond red glasses (with 35Y) at the Bureau is an additive one within the tolerances considered satisfactory for calibrating glasses to be used in the grading of vegetable oils. The 2,300 Lovibond red glasses already submitted for calibration have been graded in terms of this additive scale, the values reported being stated (in each report) to have a maximum uncertainty of 0.1 for N less than or equal to 10.0, of 0.2 for N greater than 10.0 but equal to or less than 16.0, and of 0.4 for N greater than 16.0.

It is desirable, not only that the scale be additive as already defined and illustrated, but also that the same value of N'' be obtained, whether by way of spectral transmission measurements and computation of r/g ($N''_{r/g}$) or by direct comparison with the Bureau's standard glasses (N''_{obs}).

[27] The spectral transmissions of these glasses are published in BS Sci. Pap. S547.
[28] See BS Research Pap. RP653.

The first test of this kind was made upon the red glasses of BS test 41,960, previously noted. The discrepancies between N''_{obs} and $N''_{r/g}$, in only one case exceeding 0.06 (0.10 for $N=10.0$), were not considered unduly large, since part of the discrepancy would doubtless be caused by errors in the spectral transmission.[29]

Similar comparisons of $N''_{r/g}$ and N''_{obs} were later made on 2 other groups of glasses, submitted under BS tests 59,139 and 432–1.[30] The results are shown in table 2.

TABLE 2.—*Comparison of values of N''_{obs} with values of $N''_{r/g}$ obtained from original $(r/g, N''_{r/g})$ standard curve*

[The discrepancies shown in column 5 led to the revision of the standard curve for values of N greater than 5.0, as explained in sec. V; these discrepancies were largely eliminated by this revision. There is but little correlation between values of $N''_{obs}-N''_{r/g}$ and values of $P-P_{N''}$]

1	2	3	4	5	6
Designation of glasses	N	N''_{obs}	$N''_{r/g}$	$N''_{obs}-N''_{r/g}$	$P-P_{N''}$
BS test 59,139	2.0	2.42	2.40	+0.02	+0.0005
	4.0	4.30	4.22	+.08	−.0015
	6.0	6.34	6.25	+.09	−.0008
	10.0	10.52	10.35	+.17	−.0032
BS test 432–1	.10	.16	.19	−.03	+.0002
	.20	.29	.28	+.01	+.0004
	.30	.46	.42	+.04	+.0001
	.40	.57	.56	+.01	+.0001
	.50	.63	.62	+.01	−.0009
	.60	.73	.72	+.01	+.0001
	.70	.82	.81	+.01	+.0004
	.80	.92	.93	−.01	−.0002
	.90	1.04	1.05	−.01	+.0002
	1.0	1.24	1.30	−.06	−.0003
	2.0	2.25	2.25	.00	+.0001
	3.0	3.32	3.35	−.03	.0000
	4.0	4.25	4.24	+.01	−.0026
	5.0	5.48	5.43	+.05	−.0020
	6.0	6.32	6.28	+.04	−.0023
	7.0	7.20	7.08	+.12	−.0022
	8.0	8.57	8.47	+.10	−.0033
	9.0	8.99	8.94	+.05	−.0018
	10.0	10.41	10.28	+.13	−.0020
	20.0	21.72	20.98	+.74	−.0006

An examination of these data (including also those of test 41,960 which are not shown) indicated that no important discrepancy existed between the values of N''_{obs} and $N''_{r/g}$ for values of $N=0.1$ to $N=3.0$. From $N=4.0$ to $N=10.0$ (and 20.0), however, there was shown an increasing tendency for the values of $N''_{obs}-N''_{r/g}$ to be positive, this discrepancy in some cases exceeding the maximum uncertainty of 0.1 (or of 0.4 for $N=20.0$) given in the reports made on glasses submitted for calibration.

From table 2 it might be suspected that the differences, $N''_{obs}-N''_{r/g}$, were related to some extent to the purity deviations, $P-P_{N''}$, since a tendency may be noted for the largest positive values of the former to group with the largest negative values of the latter. However, computation (including data on the glasses of test 41,960) shows

[29] The magnitude of the differences in $N''_{r/g}$ to be expected from errors in spectral transmission is illustrated in the appendix, p. 449.

[30] Acknowledgment is made to D. B. Judd and Mabel E. Brown for assistance in securing the data of this test.

this correlation to be only 20 percent, approximately, with a probable error half as large. Since the discrepancies between N''_{obs} and $N''_{r/g}$ can be adequately explained otherwise (see next section), it may be concluded that there is no important relation between these discrepancies and the purity deviations.

The question of purity tolerances may, however, be considered in this connection. Four glasses have been found with values of $P-P_{N''}$ greater than -0.0050, the maximum being -0.0066. In none of these cases did the values of $N''_{obs}-N''_{r/g}$ exceed $+0.05$. This further illustrates the lack of correlation between these quantities and shows that the question of purity tolerances has proved of little importance in connecton with the 2,300 glasses already graded.

No specific tolerances have, therefore, been fixed for the values of $P-P_{N''}$. However, it seems undesirable that this quantity exceed 0.005. Such a value is two or three times the least difference perceptible with our conditions of observation and makes the determination of N''_{obs} relatively difficult. None of the 78 calibrated glasses of BS 9940 has a value of $P-P_{N''}$ greater than 0.0036, and the values for the standards selected for use in the grading of glasses submitted for calibration do not exceed 0.0012.

V. REVISION OF THE (r/g, N'') STANDARD CURVE

Since the values of table 2 were based on extensive and repeated measurements, it seemed necessary to reexamine the standards of higher value used in the determination of N''_{obs}. Such redetermination did not have as a purpose the assignment of new values of $N''_{r/g}$ to the standards. This was unnecessary because the scale had been shown in various ways to be additive to the desired degree (see sec. III), and was highly undesirable because of the large number of glasses that had already been graded in terms of these standards. The purpose was (1) a remeasurement of the spectral transmissions [31] of the higher-valued working standards, (2) a recomputation of r/g to see if the larger discrepancies would be reduced, (3) if so, an empirical revision of the (r/g, N'') curve of such kind if possible that the same values of $N''_{r/g}$ would be obtainable with the new values of r/g. Such revision would be based also on the values of N''_{obs} (table 2) for which accurate values of r/g were also available. This would further insure the continued additivity of the scale and for values of N greater than 10.0 put it on a more certain basis than before.[32]

In table 3 is summarized all the data entering into the reexamination and revision of the (r/g, N'') curve. The values are plotted in figure 3. It was highly desirable, as stated above, that the values of $N''_{r/g}$ originally assigned the standard glasses remain unchanged. Hence the new values of r/g are plotted against the original values of $N''_{r/g}$. In the case of the standards, $N=12.0$, 13.0, 17.0, and 20.0, the values of r/g are also plotted against the values of N''_{obs} obtained for these 4 glasses by the regular method of comparison and grading in terms of standards having values of N'' equal to 10.0 or less.

[31] Improved apparatus and technique gave expectation that more accurate values would be obtained. (See Appendix.)

[32] It was originally intended not to accept glasses for calibration having values of N greater than 10.0. While the original standardization of the glasses of BS 9940 included all the exact integer glasses from 10.0 to 20.0, there had never been any extensive experimental tests of the additivity of the scale in this region.

TABLE 3.—*Data on which is based the revision of the* (r/g, $N''_{r/g}$) *standard curve*

1	2	3	4	5	6	7
Designation of glasses	N	$N''_{r/g}$ (original calibration)	r/g (1930–31)	N''_{obs}	Deviation from corrected curve for	
					$N''_{r/g}$	N''_{obs}
	0.86	1.003	1.1558	.....	−0.02	.....
	1.8	1.95	1.2149	.....	−.03	.....
	2.8	2.99	1.2766	.....	+.03	.....
	3.9	3.94	1.3419	.....	−.01	.....
	4.9	5.08	1.4205	.....	.00	.....
	5.4	5.82	1.4721	.....	.00	.....
	5.6	6.16	1.4994	.....	−.04	.....
	6.0	6.531	1.5224	.....	.00	.....
Standards of BS 9940	6.8	6.85	1.5466	.....	−.01	.....
	7.6	7.59	1.5982	.....	+.03	.....
	8.2	8.04	1.6376	.....	−.06	.....
	9.0	9.171	1.7174	.....	.00	.....
	9.8	10.00	1.7830	.....	−.04	.....
	12.0	12.168	1.9434	12.19	.00	+0.02
	13.0	12.983	2.0023	12.92	+.02	−.04
	17.0	17.125	2.3094	17.22	−.03	+.06
	20.0	19.670	2.4994	20.05	−.22	+.16
	.10	.....	1.1069	.16	.....	−.02
	.20	.....	1.1122	.29	.....	+.01
	.30	.....	1.1203	.46	.....	+.04
	.40	.....	1.1286	.57	.....	+.01
	.50	.....	1.1321	.63	.....	+.01
	.60	.....	1.1376	.73	.....	+.01
	.70	.....	1.1427	.82	.....	+.01
	.80	.....	1.1498	.92	.....	.00
	.90	.....	1.1570	1.04	.....	.00
	1.0	.....	1.1717	1.24	.....	−.04
BS test 432-1	2.0	.....	1.2311	2.25	.....	.00
	3.0	.....	1.3022	3.32	.....	−.02
	4.0	.....	1.3618	4.25	.....	+.01
	5.0	.....	1.4464	5.48	.....	+.03
	6.0	.....	1.5084	6.32	.....	−.01
	7.0	.....	1.5676	7.20	.....	+.05
	8.0	.....	1.6704	8.57	.....	+.03
	9.0	.....	1.7053	8.99	.....	−.03
	10.0	.....	1.8088	10.41	.....	+.03
	20.0	.....	2.6208	21.72	.....	.00
	2.0	.....	1.2405	2.42	.....	+.02
BS test 59,139	4.0	.....	1.3611	4.30	.....	+.07
	6.0	.....	1.5061	6.34	.....	+.04
	10.0	.....	1.8141	10.52	.....	+.07
BS test 62,704-L	20.0	.....	2.6091	21.55	.....	.00
Alg. mean (N=1.0 to N=20.0, excluding N=20.0, BS 9940)	.....	.....	.....	.....	−.00[5]	+.01[5]

For the respective test glasses the values of r/g are plotted against the values of N''_{obs}. Provided the values for the test glasses are found to plot consistently with those for the standards, the resulting curve will satisfy the various requirements that have been noted, viz:

1. It will be on the average in accord with the values of $N''_{r/g}$ originally assigned to the standards of BS 9940.
2. It will be additive, inasmuch as it will be consistent with values of N''_{obs} over the whole range.
3. Values of N'' obtained via spectral transmission and computation will closely check those obtained by direct observation.

In figure 3 the dotted curve represents the original (r/g, N'') curve shown in figure 2. The continuous line is the empirically corrected curve, drawn to fit the plotted points as accurately as possible. However, no correction was considered necessary for values of N'' less than 5.0, and the 2 curves deviate perceptibly only above this value.

In table 3, columns 6 and 7, are shown the deviations of the plotted values from the corrected curve. The following points may be noted:

1. None of the values of $N''_{r/g}$ assigned to the standards, nor of N''_{obs} obtained by comparison with the standards, deviate from the corrected curve by more than ± 0.07, excepting only $N=20.0$, BS 9940.

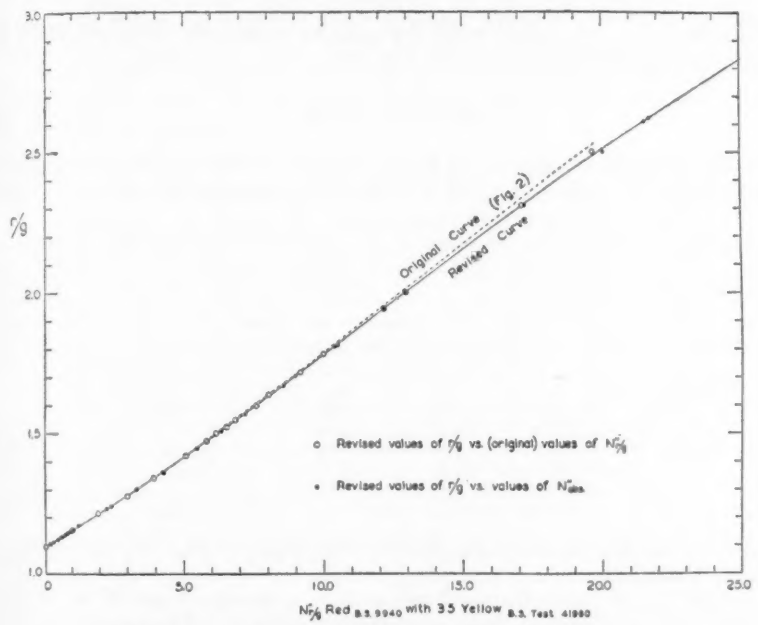

FIGURE 3.—*Revision of standard* (r/g, $N''_{r/g}$) *curve.*

Data taken from table 3.

2. The deviations, without any exception, fall within tolerances adopted as satisfactory for grading Lovibond red glasses with 35 yellow. These tolerances have been stated at the beginning of section IV.

3. As shown by the algebraic means of the deviations (columns 6 and 7), the average discrepancy between the values of $N''_{r/g}$ and N''_{obs} is less than 0.03. ($-0.00_9-0.01_5=-0.02_4$.)

4. By use of this corrected curve, essentially the same values of N'' may be obtained from accurate spectrophotometric measurements as are obtained by direct comparison with the standards of BS 9940.

5. The values in column 7 of table 3 compared with the values for the same glasses given in the fourth column of table 2 show the improvement effected at the higher values by the corrected curve.

VI. REPRESENTATIVE NATURE OF THE N'' UNIT AND SCALE

It has already been shown[33] that on the basis of the first 1,000 glasses graded, the relation between the N and N'' scales may on the average be expressed by the least-squares equation

$$N''=1.02N+0.14 \tag{3}$$

If the equation be derived on the basis of only those glasses which have values of $N=1.0, 2.0, 3.0, \cdots 20.0$, the following is obtained:

$$N''=1.014N+0.21 \tag{4}$$

This may be compared with the similar equation obtained with the 20 glasses of BS 9940 ($N=1.0, 2.0, 3.0, \cdots 20.0$):

$$N''=0.987N+0.26 \tag{5}$$

A comparison of equations 4 and 5 shows a significant difference in the average N'' values for the 2 cases, as illustrated in table 4. These

TABLE 4.—*Comparison of values of N'' computed from equations 4 and 5*

N	N''		
	Equation 4	Equation 5	4 minus 5
0.0	0.21	0.26	−0.05
1.0	1.22	1.25	−.03
1.85	2.09	2.09	.00
5.0	5.28	5.20	+.08
10.0	10.35	10.13	+.22
20.0	20.49	20.00	+.49

values show the important differences that exist for values of N greater than 5.0.

Of still more importance, however, is a comparison of the values of $\Delta N''/\Delta N$ as derived from equations 4 and 5. These values, that is, the slopes of the lines represented by the equations, are respectively 1.014 and 0.987, and the ratio of the first to the second is 1.027. In other words, the average N'' difference between the adjacant glasses in the series $N=1.0, 2.0, 3.0, \cdots 20.0$ is 2.7 percent greater for the tested glasses than for those of BS 9940. Therefore, if the N' value of the nominal unit glass had been derived in the same manner and with the same values of N as given in table 1, but with glasses representative of the averages found for the tested glasses, this N' value would have approximated $1.173/1.027=1.142$, instead of the value 1.173 obtained from the 20 glasses of BS 9940. Equation 3 would, in this case, have been:

$$(N'')=(1.02/1.027)N+0.14/1.027=0.993N+0.14. \tag{6}$$

On the average the values of N'' and N for the first 1,000 glasses would then have been more nearly alike for the larger values of N.

[33] BS Research Pap. RP653.

For small values of N, however, this change in the unit would produce but little change in the values of N''. For this region, the observed differences between N'' and N are due mostly to lack of additivity in the average N scale, as exemplified by the intercepts of the equations, that is, the values of N'' when $N=0$. (See RP653, p. 279 to 282.) No change in the magnitude of the unit would effect any appreciable improvement in this respect.

It is in no way surprising that the 20 glasses of the Bureau set, BS 9940, fail to give exactly the same scale and unit that a much larger number of glasses would have given. The slight failure of the Bureau glasses to be accurately representative of the first 1,000 glasses graded has apparently caused no trouble or inconvenience to the oil trade, whereas the elimination of the erratic and consistent deviations from additivity that existed among the Lovibond red glasses when combined with 35Y has removed one of the principal causes of dispute regarding the color grading of cottonseed oils. The Priest-Gibson (N'') scale may now be considered as thoroughly established in America.

APPENDIX

EFFECT OF SPECTROPHOTOMETRIC UNCERTAINTIES

The question arises as to whether the differences between the values of r/g obtained for the standards in 1930 and those obtained earlier (1924–28) are due to changes in the glasses or to errors in the determinations of their spectra transmissions. It is believed the latter is the cause, inasmuch as adequate reasons are known for the discrepancies. The differences in the two determinations of spectral transmission may be put into 2 classes:

1. Those caused by ordinary experimental error. It has previously been pointed out [34] that the Lovibond glasses are imperfect optically. Striae, bubbles, and pits are usually present in varying degree and there is known to be in some cases a slight variation of color over the surface of the glass. For glasses of such optical condition, highly accurate measurements cannot be made, and errors or uncertainties as large as 1 percent of the transmission are to be expected. A total discrepancy of 2 percent between 2 determinations is, therefore, not considered excessive. This limit was rarely exceeded at any wave length for any of the 17 standards listed in table 3, excepting 1 glass, $N=9.0$, where a bubble in the center of the glass was apparently the cause of the earlier values averaging 3.0 percent lower than the later ones, and excepting the glasses, $N=12.0$,13.0, 17.0, and 20.0 at 500 to 550 mμ, which are discussed below. It is quite certain that the recent determinations are more accurate than the previous ones; the spectrophotometric technique has been improved, and from 2 to 4 complete sets of measurements were made on each glass in the recent determination as compared to only 1 (in most cases) in the previous determinations.

2. Those ascribed to special instrumental error. The glasses having values of $N=12.0$ to $N=20.0$ show consistent discrepancies in the region of maximum absorption, viz, from 500 to 550 mμ, the discrepancies increasing as N increases. The earlier values were lower than the recent ones, thus causing the r/g values to be higher. These relatively large discrepancies from 500 to 550 mμ may be certainly ascribed to instrumental error in the 1923 measurements. The apparatus was at that time as described in BS Sci. Pap. S440. For the recent measurements, the apparatus was as described in BS Research Pap. RP30. Among other improvements was the installation of auxiliary rotating sectors of accurately known aperture. For low transmissions, where the nicol readings are otherwise too near the extinction points, a sector of 10 or 1-percent aperture is now used in the blank beam and the transmission of the glass measured relative to that of the sector. This brings the nicol readings back into a part of the scale known to be accurate by measurements made on sectors of higher transmission.[35] These

[34] BS Sci. Pap. S547, p.14.
[35] For further discussion and illustration of this point, see BS Research Pap. RP30; also J.O.S.A. **21**, 564 (September 1931).

auxiliary sectors were used at low transmissions in all the recent measurements, so that in the region of lowest transmission, 500 to 550 mμ, the discrepancies found should be due mostly to errors in the previous measurements.

TABLE 5.—*Differences in r/g and $N''_{r/g}$ caused by differences in spectral transmission obtained in 2 different determinations*

[A refers to first determination, B to second determination]

N	$(r/g)_A-(r/g)_B$	$\Delta(N''_{r/g})$	N	$(r/g)_A-(r/g)_B$	$\Delta(N''_{r/g})$
0.86	−0.0017	−0.03	7.0[a]	−0.0032	−0.04
1.8	−.0026	−.05	7.6	+.0070	+.09
2.0[b]	+.0013	+.02	8.0[a]	−.0030	−.04
2.8	+.0027	+.02	8.2	+.0006	.00
3.9	−.0003	.00	9.0	+.0058	+.07
4.0[a]	−.0029	−.05	9.0[a]	−.0052	−.07
4.0[b]	+.0004	.00	9.8	+.0044	+.05
4.9	+.0010	+.01	10.0[a]	−.0047	−.06
5.0[a]	−.0048	−.06	10.0[b]	−.0053	−.06
5.4	+.0024	+.03	12.0	+.0120	+.15
5.6	+.0001	.00	13.0	+.0149	+.18
6.0	+.0046	+.06	17.0	+.0247	+.33
6.0[a]	+.0022	+.03	20.0	+.0254	+.35
6.0[b]	−.0030	−.03	20.0[a]	−.0244	−.33
6.8	+.0041	+.05			
			Arith. Mean (N=0.86 to 10.00) =		0.03 [a]

[a] BS test 432-1;
[b] BS test 59139;
Other values, BS 9940.

In table 5 are shown the differences in r/g obtained from the 2 sets of spectrophotometric measurements and the differences in $N''_{r/g}$[36] equivalent to these differences in r/g. These values are given not only for the standards of BS 9940 but also for certain other glasses upon which 2 complete sets of spectral transmission measurements had been made. Values of $\Delta(P-P_{N'})$ in no case exceed ± 0.0011.

It seems apparent from table 5 that uncertainties in $N''_{r/g}$ resulting from our spectrophotometric data, for values of N not greater than 10.0, are less than 0.1. The average discrepancy is about 0.04. We believe that possible errors in values of $N''_{r/g}$ determined from present spectrophotometric data obtained in the colorimetry section will not exceed ± 0.05. Without due regard to the various considerations necessary to insure accurate spectrophotometric work, however, considerably larger errors than those illustrated may result. The four glasses of BS test 59,139, table 5, were measured in another laboratory. The following discrepancies were obtained between values computed from their published curves, subscript C, and from our second determinations:

N	$(r/g)_C-(r/g)_B$	$\Delta(N''_{r/g})$
2.0	−0.0005	−0.01
4.0	+.0073	+.11
6.0	+.0225	+.31
10.0	+.0425	+.54

These values compared with those for the same glasses in table 5 show the relatively large errors that may be obtained from inaccurate spectrophotometric measurements.

The question arises also as to why the $N''_{r/g}$ values originally obtained for the glasses of BS 9940 (having values of N=1.0, 2.0, 3.0, . . . 20.0) in the derivation of the Priest-Gibson scale in table 1 are additive, as shown by the revised

[36] It should be remembered that the value of $N''_{r/g}$ was not changed for any of the standard glasses (see section V); the values of $\Delta N''_{r/g}$ in the case of the standards merely show the differences in $N''_{r/g}$ that are equivalent to the differences in r/g obtained in the 2 determinations.

curve of figure 3, when the higher valued glasses have been found to have significant errors in the original spectral transmission measurements. The answer seems to be that these errors were more or less consistent and caused errors in the values of r/g which were roughly proportional to N. This is shown in figure 4 where the values of $(r/g)_A-(r/g)_B$ (table 5) are plotted for those glasses of BS 9940 which entered into the derivation of the scale in table 1, viz., $N=6.0$, 9.0, 12.0, 13.0, 17.0, and 20.0. A straight line drawn through these values intersects the abscissa at $N=5.0$ approximately instead of $N=0$; however, the rough

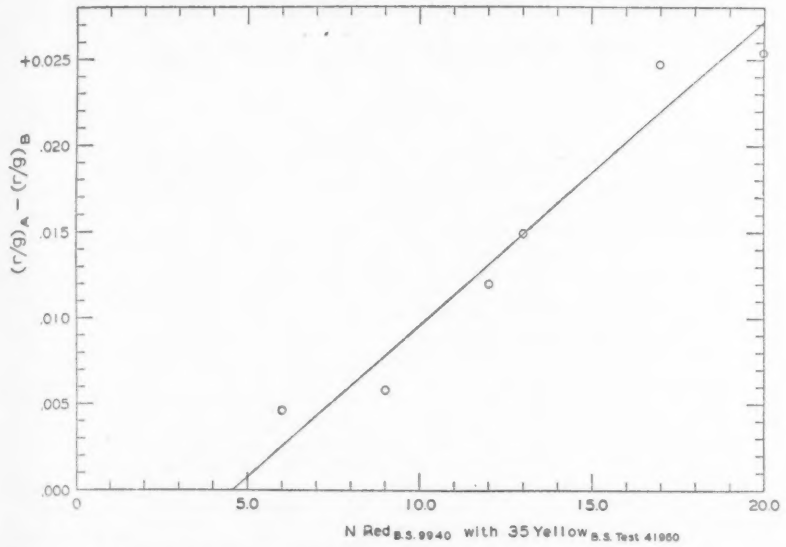

FIGURE 4.—*Relation between values of N and the discrepancies in r/g for certain glasses of BS 9940.*

proportionality shown for values of N greater than 5.0 is believed to afford adequate explanation of the question raised at the beginning of this section, since the r/g curve is nearly straight between $N''=5.0$ and $N''=20.0$. It is interesting to note that the revised curve in figure 3 deviates from the original curve only for values of N'' greater than 5.0.

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ETHER-INSOLUBLE OR GEL RUBBER HYDROCARBON, ITS SOLUTION, CRYSTALLIZATION, AND PROPERTIES

By W. Harold Smith and Charles Proffer Saylor

ABSTRACT

A method was previously described for purifying the hydrocarbon in Hevea latex and separating it into two fractions by extraction with ethyl ether. The present paper deals with the insoluble (commonly called the gel) fraction, of which about one-fourth of the total hydrocarbon is composed. Presumably the gel is insoluble in ether because of a complex structure and high molecular weight. When traces of oxygen are present, it becomes soluble in suitable organic liquids. The dissolved gel was crystallized from a dilute solution at low temperatures, and the crystals were examined. The refractive indices, $\epsilon = 1.535$ at $-5°$ C, and $\omega = 1.583$ at $-5°$ C, are very close to the values previously found for crystals of ether-soluble hydrocarbon. Melting temperatures, which lie somewhere between $-5°$ C and $+14°$ C, depend upon the history of the sample and indicate that the crystals are solid solutions, probably of many closely related components. As witnessed by micromanipulation below their melting temperature, the gel crystals contrast sharply in elasticity with the crystals of sol rubber. The former appear to be elastic, the latter are plastic. Also, after the loss of birefringence indicates that the crystals are melted, the gel is more resistant to deformation than the sol. Crystals of ether-soluble rubber have been vulcanized below their melting point by means of sulphur chloride. The shape of the crystals remains unchanged, but birefringence, the optical evidence of crystallinity, disappears, and their resistance to deformation is increased.

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I. PREPARATION AND CRYSTALLIZATION OF GEL RUBBER HYDROCARBON

By W. Harold Smith

1. PREPARATION OF THE GEL

A method of purifying and crystallizing ether-soluble rubber hydrocarbon was described in an earlier paper in this journal.[1] The same

[1] BS J.Research **10**, 479(1933); RP544. In the earlier paper the portions into which rubber is separated by ethyl ether were called the ether-soluble and the ether-insoluble fractions. To conform to common usage, the fractions will also be called sol and gel, and these terms refer specifically to fractions which have been purified and separated as described in the earlier paper. The use of these terms does not imply that the sol does not dissolve to form a true solution at the temperature and concentration which prevail during crystallization. They are used as names and do not necessarily refer to the sol and gel states of matter as defined by colloid chemistry.

procedure for purifying the hydrocarbon and separating it into two fractions was followed in the preparation of the insoluble or gel fraction, the properties of which are the subject of this paper. The method of purification was not merely another procedure for removing the impurities from rubber hydrocarbon, but, as stated in the earlier paper, it also "sought to maintain unchanged the structure of rubber hydrocarbon and to permit a sharp separation of the ether-soluble and insoluble fractions."

The latex which has been used was, in part, obtained from Harry L. Fisher of the United States Rubber Co. Through the courtesy of the U.S. Department of Agriculture, latex has also been obtained direct from the plantation on the north shore of Haiti. Before the trees were tapped, the area surrounding the intended incision was carefully cleaned. After tapping commenced, the trees were tapped once each day, the latex from the first two tappings was rejected, and that obtained on the third day was put into clean glass bottles, which were filled completely after the addition of a little ammonia as stabilizer. The latex was immediately shipped to this Bureau and stored at a temperature maintained between 0 and 2° C.

Briefly, the rubber hydrocarbon was prepared as follows. Latex of *Hevea brasiliensis* was dialyzed and the protein removed by tryptic digestion in the presence of natural antioxidants, which had been extracted from crude rubber and which were added to the latex at intervals. The purified hydrocarbon was separated into two fractions by thorough continuous extraction with ethyl ether in an apparatus constructed entirely of glass and similar to that described by Pummerer, Andriessen, and Gündel.[2] Oxygen in the apparatus was displaced by a continuous stream of nitrogen of 99.8 to 99.9 percent purity. The nitrogen was under slight pressure, and to facilitate the exclusion of air all joints were covered with a film of glycerol. The rigid exclusion of oxygen is necessary because the presence of even a minute amount of it causes the gel to dissolve slowly and makes a sharp separation impossible. It is advantageous to have an antioxidant in the solution during the extraction, and either the natural antioxidants or phenyl-β-naphthylamine was used. With these precautions against oxidation, it was possible to separate the rubber into the two fractions rather sharply.

The manner in which oxygen causes the insoluble gel fraction to become soluble is not understood. Oxygen adsorbed by the rubber, or a trace of an oxygen addition product of rubber such as that formed by auto-oxidation, or a trace of acid formed by oxidation may peptize the gel in suitable organic solvents. In a typical experiment with 50 g of total rubber the extraction was continued beyond the point at which it is normally considered to be complete. One week of continuous extraction was required. The final extract was removed, a fresh supply of ether, which had been previously saturated with nitrogen, was added to the rubber, and the extraction was continued for 72 hours longer. The extract contained 20 mg of rubber, or 0.04 percent of the original sample. The swollen gel rubber which remained after extraction was desolvated with acetone, and residual ether and acetone were removed in vacuo. If it was necessary to preserve the gel fraction for an interval, it was cut into suitable small

[2] Ber. Deut. Chem. Ges. **60B**, 1583(1928).

pieces and allowed to remain for 24 hours in an acetone solution of the natural antioxidants or of phenyl-β-naphthylamine. The acetone was removed in vacuo, and the gel was placed in a desiccator which was evacuated and filled with nitrogen several times. Before the gel was put to any use, the antioxidants were removed by extraction with acetone.

In the extraction of numerous samples of latex, about the same proportion of gel, 25 percent of the original hydrocarbon, was always obtained. Other observers have reported very divergent proportions, ranging from 0 to 70 percent, in rubber of various kinds extracted with different solvents.

The quantitative determination of sol and gel in the total rubber by extraction with ether must be conducted in the absence of oxygen. A small Soxhlet extractor, suitably modified to allow a continuous stream of nitrogen to pass through it during the extraction, was used. The upper outlet of the extractor, above the condenser, was connected to a flask through which an auxiliary stream of nitrogen was constantly passed and the outlet of the flask consisted of a mercury bubble trap. To avoid prolonged extraction, samples weighing about 1 gram were used. They were first extracted with acetone to remove antioxidants and the weight of the sample was corrected for acetone-soluble material. After the excess acetone was siphoned from the rubber, ether was added to remove residual acetone and immediately siphoned away. Sufficient ether was added to cover the rubber, the flask was cleaned and filled with ether, the apparatus assembled, and nitrogen was passed through it. The rubber was allowed to swell to a maximum before the extraction with ether was started. During the extraction, fragments of the swollen gel tended to become detached and to be swept out with the extracted material. The rubber was therefore placed in a container of no. 100 platinum gauze of sufficient size to permit the rubber to swell to its maximum volume. The approximate time necessary to extract the soluble fraction was determined on a separate sample by weighing successive extracts. The last traces of soluble material were removed with difficulty from the swollen gel. When the extraction was complete the ether was removed from each fraction in vacuo and the residues were dried in vacuo to constant weight. Each fraction was corrected for ash.

The mean of six determinations, which were obtained after some familiarity with the details of the method was acquired, indicated a sol content of 75.3 ± 0.8 percent and a gel content of 24.2 ± 0.7 percent. Probably a little gel was dissolved during the extraction and the results represent only an approach to the true value.

2. SOME PROPERTIES OF SOL AND GEL

Some investigators who purified rubber by methods other than the one which is used in this work, noted differences in the soluble and insoluble fractions. The fractions of rubber, as separated in this investigation, show marked differences. The sol can be stretched or otherwise deformed more than the gel and by smaller forces, and it can be readily masticated on a rubber mill. The gel is tough, resistant to mastication, and may be described as gristly. No quantitative study of the physical properties of the unvulcanized fractions has yet been made.

A sol-gel reversible transformation has been attributed to rubber on the assumption that a single chemical compound is concerned. The data which follow on the melting points of crystals obtained from the gel after it has become soluble in ether indicate that the soluble gel is not the same hydrocarbon that is in the ether-soluble fraction of total rubber hydrocarbon. Consequently the gel and sol, as these terms are here used, are not merely different phases of the same molecular species.

Porritt [3] observed that gel was formed in a rubber solution which was sealed in glass and exposed to sunlight. When the container was opened the gel became soluble. A similar effect in a solution of ether-soluble rubber has been noted by the author. (See footnote 1.) There is no evidence that the gel formed in the sealed tube is identical with that left after the original extraction of the rubber with ether. The conversion of the sol to a gel has not yet been investigated by an examination of the crystals.

3. DISSOLVING AND CRYSTALLIZING THE GEL

The gel was dissolved in an organic solvent by permitting the entry of a little air and, depending upon the amount of air used, temperature, and other conditions, the time required completely to dissolve the gel could be varied from a few weeks to several months. Ethyl ether, ethylbenzene, or toluene was generally used because it remains liquid under the conditions of crystallization. Inorganic constituents of the latex, which concentrate in the gel when the soluble fraction is extracted, remain undissolved by the organic solvent.

It is evident from the preceding discussion that the gel fraction is separated from the sol by its insolubility in ethyl ether and that subsequently it is dissolved in ethyl ether. Organic compounds of high molecular weight tend to be less soluble in the inert solvents than their simpler homologs. The solution of the gel probably contains the products of disaggregation of a more complex structure which exists in the insoluble gel.

Suitable conditions for the growth of crystal nuclei of ether-soluble rubber hydrocarbon and the establishment of their crystal habit were discussed in the earlier paper. (See footnote 1.) The same technic was used to obtain crystals of the dissolved gel fraction. When hydrocarbon solvents were used, they were customarily diluted with anhydrous ethyl ether before crystallization of the rubber, as this medium has greater fluidity and therefore insures greater mobility of the nuclei than hydrocarbon solvents alone. One volume of a hydrocarbon solution of rubber diluted with four volumes of ethyl ether is suitable, but these proportions may be varied considerably. For studies of the optical properties and melting point, the dissolved gel hydrocarbon was crystallized from ethyl ether or a mixture of ethylbenzene and ethyl ether.

The particles which appeared in the solution at low temperature were birefringent under crossed nicols, and nodules formed on the walls of the container when proper supersaturation existed in the solution, a behavior similar to that observed with ether-soluble rubber hydrocarbon. Between 90 and 95 percent of the rubber in the solution separated as crystals.

[3] India Rubber J. 60, 1161(1920).

The optical properties of the crystals were studied with deposits made in the special cell which was described in the earlier paper. (See footnote 1.) The following technic was developed to permit the study of several crystalline deposits obtained simultaneously from a single solution. A vertical glass support was provided with glass brackets to hold a succession of cover glasses and the support was placed in a 12-in. test tube which contained the solution of gel rubber. Two cover glasses were placed on each bracket to prevent the deposition of crystals on the under side of the upper cover glass—the one which was subsequently observed. After crystallization was accomplished, the ethereal solution was removed at low temperature through a siphon and the crystals were washed with acetone at a temperature below the melting points of the crystals, which was then similarly removed. After washing with cold acetone several times, a cold solution of calcium chloride was poured into the tube. A cover glass was quickly removed from the rack when required and placed in a cold solution of calcium chloride under the objective of a microscope.

A supplementary method of obtaining crystalline rubber has been observed. If a lump of pure sol rubber, or of gel rubber which previously has been made soluble, is placed in cold ether and the temperature maintained at −55 to −60° C, crystals are produced. The solubility under these conditions is sufficient to permit a continuous deposition of crystalline hydrocarbon. This technic is commonly used by the crystallographer and it may offer a means of producing crystalline rubber in greater quantity than can be readily obtained from previously prepared solutions. Aside from establishing the crystallinity of the deposits by their appearance when viewed between crossed nicols, no detailed study of their optical properties was made.

The effect of a trace of trichloroacetic acid or of a mineral acid in a solution of total rubber is well known to rubber chemists. The viscosity of the solution is lowered and a profound change occurs in the structure of the rubber. Sunlight accelerates these changes. Gel rubber hydrocarbon was dissolved in ethylbenzene which contained 0.05 percent of trichloroacetic acid. When it was completely dissolved the acid was removed, and the rubber hydrocarbon in a solution of suitable concentration was subjected to the conditions for obtaining crystals. A deposit was obtained which was found to be crystalline when viewed between crossed nicols. The initial products of disaggregation can therefore be crystallized.

4. COMPOSITION OF THE GEL CRYSTALS

Crystalline hydrocarbon obtained from the dissolved gel fraction was analyzed by Henry J. Wing to determine the ratio of hydrogen to carbon. The apparatus described in Research Paper RP544 was used and the ratio was established by the criteria discussed in that paper. It was necessary to heat carefully when removing traces of solvent from the rubber. To effect this, the sample was placed in a small glass chamber and heated to 100° C by a glycerol bath. A low pressure was maintained by a mercury vapor pump. It was observed that the ether-insoluble material obtained by crystallization was more susceptible to decomposition, as indicated by discoloration and an odor of oxidation products, than ether-soluble rubber obtained similarly. Attempts to prepare suitable material for combustion often

failed. However, three determinations were made in which the technic was satisfactory. The ratios of hydrogen to carbon were 0.1346, 0.1346, and 0.1347, respectively and corresponded to that required by a compound of formula C_5H_8, on the assumption that the compound does not have more than 100 carbon atoms in the molecule.[4]

It will be observed in the section on the solubility and melting points of the crystals obtained from dissolved gel, that there is continuous melting of the crystals over certain ranges of increasing temperature. This suggests the possible presence of a solid solution. If a solid solution exists in the ether-insoluble fraction before it becomes soluble, the solid solution might consist either of rubber polymers of C_5H_8 of varying complexity; or it might consist wholly or in part of molecular species in which the ratio of hydrogen to carbon differs slightly from C_5H_8. The evidence favors the former condition. Should the latter exist, the variation in the composition of the crystals must be very small and it is doubtful whether analyses by combustion can disclose it.

II. MICROSCOPICAL STUDY OF THE DISSOLVED AND CRYSTALLIZED GEL

By Charles Proffer Saylor

1. HABIT AND APPEARANCE

The same apparatus [5] as previously described was employed to observe the growth of the crystals and to learn their habit. This apparatus consists essentially of a petrographic microscope, the tube of which is used in an inverted position, a special dewar flask so constructed that it has plane windows at the bottom, a cell which has plane windows at top and bottom, and tubes for emptying and filling. The cell holds about a milliliter of fluid. In addition to these, there are various structural parts and devices which provide illumination and temperature control. For further details, reference is made to the earlier article.

We frequently watched the crystals in the process of forming by filling the cell with a solution of the gel,[6] keeping it at $-50°$ C for about 1 hour, cooling to $-70°$ C for a few minutes, and then transferring it to the dewar flask for microscopical examination at low temperatures. Here for several hours it was maintained at approximately $-50°$ C. Finally, when the cell was observed between crossed nicols, bright birefringent particles began to appear. They remained suspended in the fluid and moved with the convection currents, until, growing in size and number, they clustered and settled. Finally, with some amorphous material, they covered the bottom of the cell. The crystalline masses formed in this way were not satisfactory for general observation or the determination of properties. For the purpose of shortening the time necessary to produce crystals, the amount of supercooling had been large. Too many nuclei formed, the individual crystals were too small, and the complexity of the groups obscured their component parts.

[4] BS J. Research **10**, 492(1933); RP544.
[5] Reference 1, p. 484–5.
[6] Smith prepared all of the solutions and most of the crystals whose properties are reported in this section.

Better crystals resulted when the apparatus and cycle of temperatures employed for the ether-soluble fraction (reference 1, p. 483–4) were again used. In this procedure the milder supercooling (to −65° C instead of −70° C) and the greater freedom from convection currents seem to cause formation of fewer nuclei and therefore fewer and better crystals. Even when this method was closely followed, the crystalline clumps were much less reproducible than were those obtained from the ether-soluble rubber hydrocarbon. Most frequently the nodules were badly ordered groups of birefringent particles, the individual shapes of which could not be discerned. This appearance is represented in figure 1(A). Occasionally, when only a very small part of the rubber in solution had crystallized over a long period, branching groups of needles were obtained. Sometimes there were spherical clusters formed from numerous needles radiating from a center. These, which were rarely obtained, had the same appearance as the crystals of ether-soluble hydrocarbon which were previously illustrated.[7]

2. OPTICAL PROPERTIES

A preparation in which the slender crystals radiated from a center was used for the determination of refractive indices. Needles projecting slightly from the group were used for the actual determination because they permitted greater accuracy. The liquids which matched their indices appeared satisfactory for the main body of the clumps, but the sensitivity was greater with the projecting needles on account of their isolation. The refractive indices at −5° C for light vibrating parallel and normal to the long directions of the needles were found by immersion, the method of central illumination serving as a criterion of the relation between the indices of the crystals and the immersing liquid. The immersion liquids were concentrated aqueous solutions of potassium mercuric iodide, diluted with acetone progressively until the indices of the crystals were matched. An Abbe refractometer was used to determine the indices of the immersion liquids at −5° C. As in the previous paper, and with the same reservations, the index for light vibrating parallel to the long direction of crystals has been designated as ϵ. The values

$$\epsilon = 1.533 \text{ at } -5° \text{ C}$$
$$\omega = 1.583 \text{ at } -5° \text{ C}$$

were so close to those previously reported for the crystals of ether-soluble hydrocarbon

$$\epsilon = 1.535 \text{ at } -5° \text{ C}$$
$$\omega = 1.583 \text{ at } -5° \text{ C}$$

as to lie well within the probable error of the determination. The close similarity in the optical properties of the crystals obtained from solutions of the ether-soluble and the gel portions of the rubber does not necessarily indicate identity. Members of the normal paraffins, the normal saturated higher fatty acids, and many other series show similarly close refractivities. Other properties indicate that the two fractions of rubber differ in molecular composition, but it is probable that the molecules are similarly oriented in the crystals of both and that both belong to the same homologous series.

[7] See figure 4, reference 1.

3. SOLUBILITY AND MELTING POINT

When crystals of gel rubber in contact either with the ethylbenzene-ether mother liquor, or with ether that has replaced it, are observed as the temperature slowly rises from −50° C, no change is seen until a temperature between −40 and −30° C is reached. Then through a few degrees the crystals swell with loss of birefringence, and the swollen jelly dissolves at a temperature a degree or so higher. The hydrocarbon has been so changed by or during its solution in ethylbenzene that the form which would not dissolve during continuous extraction with ether for weeks at ordinary temperatures now dissolves quickly at −35° C.

To determine the melting point of the crystals of dissolved gel rubber, many successive preparations were made. The solvent was rinsed out with numerous changes of acetone, and the melting process observed either while the crystals were immersed in acetone or after the acetone had been replaced by ethyl alcohol or a strong aqueous solution of calcium chloride. Melting was determined by the disappearance of birefringence as the temperature was permitted to rise. The melting points as found were entirely discordant. The lack of uniformity persisted when samples were prepared with scrupulous care to make them identical and when the conditions of melting were as nearly as possible the same. For this reason it was necessary to examine larger numbers of samples than was convenient with two cells of the form described. Further, it was desirable to compare the possible effect of environment upon the melting point by employing samples known to be identical, preferably by the use of several portions crystallized simultaneously from the same solution. To do this crystals were grown upon stacks of microscope cover glasses in the way described on page 457 and studied with the simple form of microscope cold stage, illustrated in figure 2.

Using this apparatus, in which the temperature rose as the liquid phase in the freezing mixture became diluted, the melting points of different portions from the same crystallization were found to check within a few tenths of a degree. This variation in the recorded temperatures may be explained by difficulties in accurately observing the beginning and end of the slow melting process. The clusters of needles are complex, which makes it difficult to know exactly when melting begins and when it is entirely ended. The elements of a cluster melt independently. They are protected from one another by the surrounding liquid and by their own resistance to movement after melting. It is possible to observe, therefore, a range of melting not merely for the entire cluster but even for some of the individual crystals of which it is composed. By examining cover glasses upon which crystals had been deposited simultaneously from the same solution, it was found that the crystals of dissolved gel rubber melt at a little lower temperature when they are immersed in acetone than when covered with an aqueous solution of calcium chloride, but that the melting interval is greater when they are immersed in the aqueous solution. Ethyl alcohol produces intermediate results. It appears from this that although acetone and alcohol are not rubber solvents, small amounts of them are dissolved by the gel rubber at temperatures above its melting point. The melting point observed when the crystals are covered by the aqueous solution must therefore be looked upon as the best value.

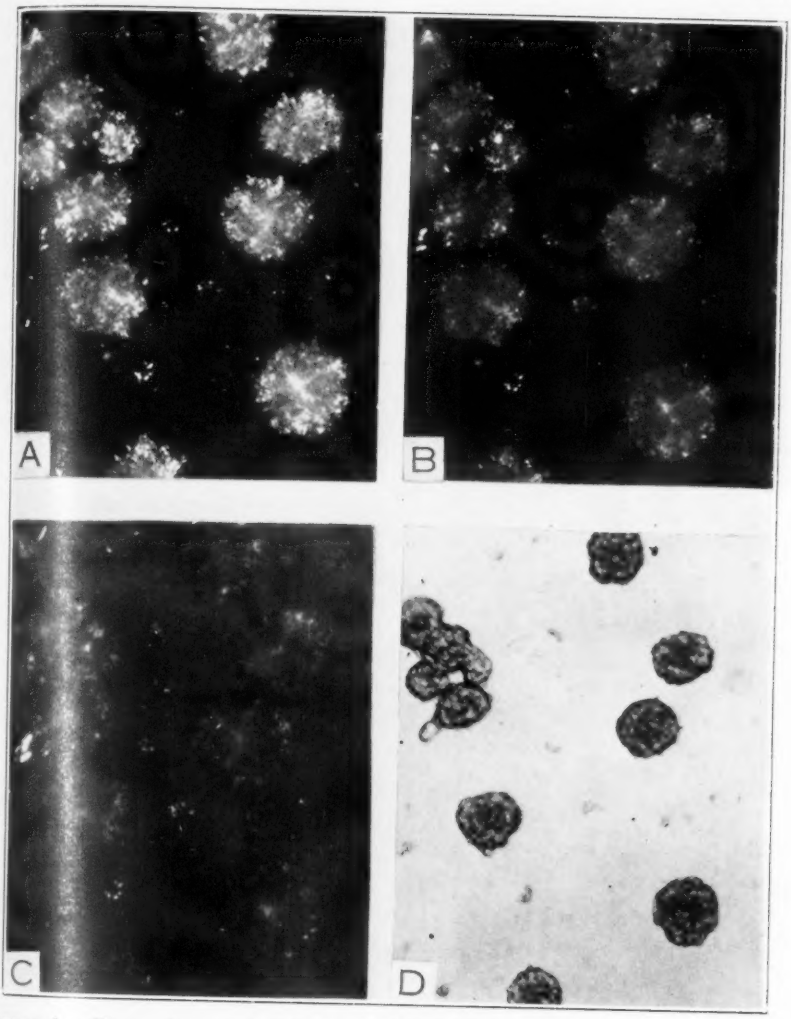

FIGURE 1.—*Photomicrographs showing melting of one sample of gel rubber crystals.*

A, Crossed nicols × 200. The mother-liquor has been replaced with acetone and the temperature allowed to rise, but the appearance of the field is not detectably changed. The brightness of the groups is caused by the optical anisotropy of the many crystals which compose them. Temperature, −6.2° C.
B, Crossed nicols × 200. The temperature has risen about four degrees. A large part of the brightness has disappeared, indicating that considerable melting has already occurred. Temperature, −1.9° C.
C, Crossed nicols × 200. Melting is nearly complete. Temperature, −0.4° C.
D, Parallel nicols × 200. After melting, surface tension has shrunken the clusters, but the large part of their structure which remains will continue indefinitely. Temperature, +0.4° C.

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When the cells were used they were well drained between applications of liquids. After withdrawing the mother liquor, the crystals were twice treated with acetone, in which they were allowed to steep for several minutes at least. They then received two treatments with aqueous calcium chloride. When the cover glasses were used, they were washed in a stream of cold acetone, steeped in acetone, washed once in aqueous calcium chloride and transferred to another portion of calcium chloride solution for the melting point determination. The melting point of a preparation treated in this way was the same as the melting point of crystals grown simultaneously from the same solution but with which the steeping in acetone had lasted more than 24 hours. This procedure differs from that described in

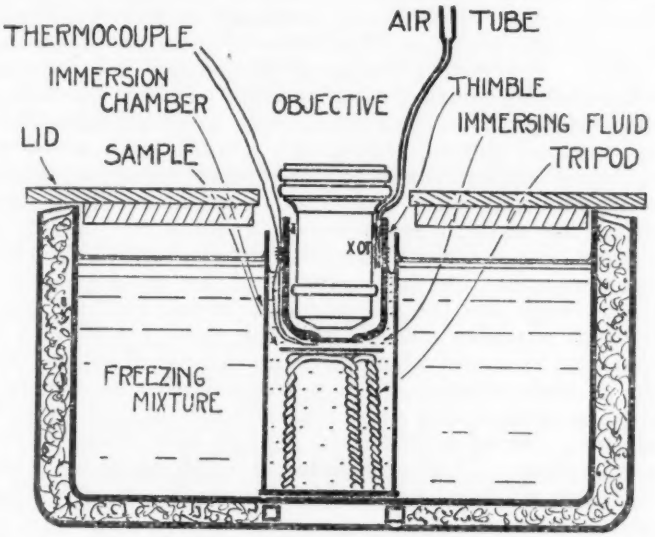

FIGURE 2.—*The simple cold stage.*

Two crystallizing dishes of slightly different sizes were chosen. Except for windows at the center of the bottom, the space between the dishes has been stuffed with rock-wool and the surfaces of the dishes silvered. The dishes are filled with a freezing mixture. Above the windows rests the immersion chamber made from a glass tube to the lower end of which is cemented a glass plate. This contains immersing fluid and a tripod of bent wire upon which the sample rests. The microscope objective dips into the immersing fluid, but is protected by a thimble made from a piece of constricted glass tubing, to the ground lower end of which is cemented a small cover glass. The thermocouple is held in place by being tied with thread to the thimble. The air tube of drawn copper tubing conducts a very slow stream of well-dried air into the space between the objective and the thimble and prevents the formation of frost. The entire apparatus rests upon the stage of a petrographic microscope

the paper on ether-soluble rubber hydrocarbon, but the results by the two methods are consonant as indicated by the melting point of 9.7 to 10.3° C found for sol crystals immersed in aqueous calcium chloride.

Even when the aqueous solution was used to surround the crystals, wide spreads were found between different preparations of crystals.[8] Sometimes melting began as low as −1.5° C and at other times not below +9.6° C. In a few experiments melting ended at +5.5° C and in others was not complete below +13.8° C. There were ranges as great as 8° C and as small as 1.2° C. The 1.2° C melting range

[8] The number of melting point determinations is too great and the significance of the variations too doubtful to justify including at this place a chronicle of them all.

was exhibited by crystals prepared in the following manner. They were grown in the cell from an ethylbenzene-ether solution. The mother-liquor was removed, the crystals were washed once with very cold ether and dissolved in more ether. From this solution crystals were again grown, the yield being small. The cell was emptied of liquid and filled twice with cold acetone and twice with a cold solution of aqueous calcium chloride. The temperature was allowed to rise and melting was observed from +4.4 to +5.6° C. Apparently fractionation was produced by the second crystallization from ether. Within the range exhibited by any preparation, the bright spots caused by the birefringence of the individual crystals disappeared sporadically, sometimes with great suddenness. In each cluster the melting was usually continuous, a crystal here and a crystal there losing birefringence without any seeming association. Individual particles sometimes continued to melt over an interval of a degree or more. Neither the melting range of the cluster nor the difference between the melting points of the crystalline particles can be explained by the assumption of delayed equilibrium or of different thermodynamic or chemical environment in the several parts of the clusters. Particles immediately adjacent to one another, separated by less than a hundredth of a millimeter, melted at temperatures differing by 5 or 6°. During the months necessary to dissolve one sample of gel,[9] crystals made from successive extracts tended to melt at progressively higher temperatures, but the character of the melting (as indicated by length of range and the independence of one another with which the individual particles melted) was the same for all and did not differ from that observed when an entire sample of gel had been dissolved in a single solution. Large irregularities in melting range, which seem to depend only upon the accidents of nucleus formation, persisted and occurred whether the gel had been dissolved in ethylbenzene or in ether. This entire behavior contrasts sharply with that of ether-soluble rubber hydrocarbon, which, when well controlled, always melted at about 10° C.

The way in which dissolved gel rubber crystals melt makes it plain that we are dealing here with no single compound. The gel rubber appears to have dissolved as a result of partial depolymerization. The separate crystals which make the clusters have different molecular compositions and are themselves almost certainly solid solutions of several different polymers. It is obviously desirable that such a mixture be separated into its constituents by fractional crystallization.

4. ELASTICITY

The simple cold stage illustrated in figure 2 made it possible to determine for the sol at least whether the crystals possess the peculiar elasticity of rubber. A striking difference between the properties of the sol and gel fractions was revealed.

Crystals of dissolved gel rubber were grown on microscope cover glasses. One of these was placed in the cold stage under aqueous calcium chloride. The rubber was present as the entangled network of crystalline needles and rods which is often obtained with the gel. While observing the crystals between crossed nicols they were manipulated with a wire. There was no plastic deformation. Instead the

[9] See p. 456.

network seemed to yield elastically. The amount and nature of the birefringence did not change, so far as could be noticed. The crystals appeared to be elastic to some degree, but it could not be fully established whether they possessed true rubber-like elasticity. The preparation was allowed to melt and the cover glass taken from the apparatus. The deposit of rubber was pressed into a ball. It had the usual physical properties of gel rubber, considerable stiffness, less extensibility than sol rubber, but also more perfect elasticity.

On the other hand, when a wire was drawn across a preparation of sol crystals, they were found to be plastic. After deformation they had strong birefringence and a new direction of extinction. A clear cover glass was pressed upon the crystalline deposit. The clusters flattened and did not recover when the pressure was released. After some crystals were melted the same experiment with the wire was tried. The rubber could not be plastically deformed, but instead the wire loosened the globules from the cover glass and pushed them aside. The cover glass was taken from the apparatus and washed with water and acetone. The deposit of rubber was rolled into a lump between the fingers. The lump possessed the customary physical characteristics of sol rubber, great extensibility but a rather large permanent set.

5. COMPARISONS OF SOL AND DISSOLVED GEL RUBBER

It was made clear on page 455 that gel rubber cannot be dissolved in ethyl ether unless some of the precautions against oxidation are abandoned. Under these conditions the ether-insoluble form becomes in some ways more like the ether-soluble rubber. The irregularity of the melting points found for the dissolved gel crystals is consistent with a partial decomposition of very large molecules in the presence of traces of oxygen—a phenomenon over which accurate laboratory control is probably impossible. The dissolved gel seems to consist of many different kinds of molecules. Most of them may still be the same as they were before. To these it may owe its peculiar type of elasticity. It may even contain some of the same molecules as predominate in the sol portion. As contrasted with the dissolved gel, the sol form seems to have suffered no decomposition. When suitable precautions against oxidation are taken, the size of the molecules is not improbably the same as it was in the rubber tree. For this reason, the appearance of the crystals tends to be about the same every time, and the same melting point is always observed.

That the gel rubber is still very different from the sol form, even after an oxygen-fostered disaggregation permits it to dissolve in ethylbenzene or in ether, is indicated by the different elastic behavior after the rubber crystals are melted. When sol rubber melts under a liquid, each nodule quickly forms a sphere with small inclusions of the surrounding liquid.[10] When the space surrounding the nodules is evacuated there form clear droplets adhering to the glass. On the other hand, when the crystals of dissolved gel rubber melt, as judged by loss of birefringence, their original shape is held almost unchanged to a temperature of 30° C or higher. There is slight deformation, but it is

[10] It must be remembered that the power of surface forces to cause deformation is much greater with substances on a microscopic scale.

not progressive and the shape is the same 24 hours later as it is after 10 minutes. The viscosity is great and the granular structure shown in figure 1 (D) is preserved. This difference between the two portions is consistent with all other data [11]—the gel has much greater stiffness and more perfect elasticity; the sol is softer, more extensible, and when deformed takes a permanent set.

By chemical action, these properties of both the sol and the gel can be changed. Thus, the crystals of dissolved gel rubber do not exhibit the more perfect elasticity after melting if they have been grown from a solution prepared by more strenuous treatment. If the gel has been dissolved by treatment with trichloroacetic acid, and crystals prepared from the solution are allowed to melt under aqueous calcium chloride solution, the clusters of crystals flow into rounded globules. This chemical action makes the gel behave more like the sol.

On the other hand, vulcanization makes the sol behave more like the gel. Sol crystals were prepared in one of the cells. The solvent was removed by washing with acetone at low temperature and all the acetone that could be siphoned was removed by that method. Always maintaining the temperature below the melting point of the crystals, a little sulphur chloride vapor was allowed to enter the cell. Much sulphur was deposited. The sulphur was dissolved with carbon disulphide at low temperature, the carbon disulphide removed with acetone, and the preparation observed with the microscope. The rubber was no longer birefringent but the original shapes of the crystalline spherulites persisted. They were pseudomorphs after the original crystals, but by combination with sulphur they had lost the molecular orientation peculiar to crystalline phases. When they were heated to 40° C there was no further change, showing that vulcanization had increased their stiffness.

The authors have appreciated the technical advice of E. W. Washburn, the late chief of the Bureau's Chemistry Division, throughout this investigation. We are indebted to Harry L. Fisher of the U.S. Rubber Company and Loren G. Polhamus of the U.S. Department of Agriculture, who supplied the latex used in this investigation.

WASHINGTON, August 21, 1934.

[11] W. Harold Smith and William L. Holt, BS J. Research **13**, 465 (1934); RP720.

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP720

Part of Journal of Research of the National Bureau of Standards, Volume 13, October 1934

VULCANIZATION AND STRESS-STRAIN BEHAVIOR OF SOL, GEL, AND TOTAL RUBBER HYDROCARBON

By W. Harold Smith and William L. Holt

ABSTRACT

Sol, gel, and total rubber hydrocarbon, prepared by a method previously described in this journal, were each compounded and vulcanized under three sets of conditions. In one case, tetramethylthiuram disulphide, a rapid accelerator of vulcanization was used. In another, triphenylguanidine, a slow accelerator was used, and in the third case the rubbers were vulcanized at room temperature by the Peachey process. The stress-strain properties of the vulcanized rubbers were determined and found to be similar for each type of cure. Vulcanized rubbers prepared from the insoluble rubber hydrocarbon were less extensible, and those prepared from the soluble rubber hydrocarbon more extensible than those prepared from the total rubber hydrocarbon.

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INTRODUCTION

The existence and significance of a soluble and an insoluble fraction in rubber hydrocarbon and the proportions in which they occur have long been the subject of conflicting reports, which have been summarized in a previous paper.[1] They were the basis of a two-phase theory of rubber structure proposed by Fessenden.[2] The history of the subject need not be reviewed here. Early knowledge of it was summarized by Engler and Herbst [3] in 1887 and an excellent historical treatment has been given by Whitby.[4]

The differing solubilities and other characteristics of the two fractions suggested a study of their behavior when vulcanized. A sufficient quantity of rubber hydrocarbon for the purpose was purified and separated into the soluble and insoluble fractions by extraction with ethyl ether, suitable compounds of each were mixed and vulcanized, and comparative tests made.

II. PREPARATION OF FRACTIONS

Purified rubber hydrocarbon was obtained from the latex of *Hevea brasiliensis* by a method previously described in this journal.[5] The main purpose of the method of purification was to separate the

[1] BS J.Research **10,** 479(1933); RP544.
[2] Sci. **20,**52(1892).
[3] Ladenburg's Handwörterbuch der Chem. **5,**479(1887).
[4] Colwyn Medal Essay. Trans. Inst. Rubber Ind. **6,**42(1930-31).
[5] See footnote 1.

fractions as sharply as possible while maintaining the structure of the rubber hydrocarbon as it exists in the latex. The purified hydrocarbon was separated into two fractions by thorough, continuous extraction with ethyl ether for several days. A stream of nitrogen was used to displace oxygen in the ether and a little phenyl-β-naphthylamine, a commercial antioxidant, was added to the ether from time to time during the separation of the fractions. The soluble fraction constitutes approximately 75 percent of the total rubber hydrocarbon, and the insoluble or gel fraction, 25 percent. The separated rubber fractions were desolvated by acetone, and the residual acetone and ether were removed from the rubber in vacuo. A little of the phenyl-β-naphthylamine which was in the ether during extraction remained in the rubber hydrocarbon, and, after the removal of the acetone and ether, an additional 1 percent of it was milled into each fraction. Whenever it was necessary to preserve the fractions, they were kept in a desiccator filled with nitrogen.

III. VULCANIZATION OF THE FRACTIONS AND RESULTS OF TESTS

Before the fractions of rubber hydrocarbon were vulcanized, the possible effect of ethyl ether, not completely removed, was determined with pale crepe. Solvents have a softening action and change the physical properties of vulcanized compounds. A sample of pale crepe was allowed to remain in contact with ether until the soluble fraction formed a very viscous solution. The ether was then removed in vacuo, and the residual rubber and a sample of the original pale crepe were compounded as follows:

Ingredients	Parts by weight
Pale crepe	100
Sulphur	3
Zinc oxide	5
Diphenylguanidine	1
Stearic acid	0.75

Samples were vulcanized simultaneously for 20 and also for 30 minutes at 142° C. For each cure, the stress-strain properties of compounds representing rubber treated and untreated with ether were alike to 600 percent elongation. There were slight but negligible differences at higher elongations. It was evident that, for the purposes of this work, the use of ether in separating the fractions did not cause differences in tensile characteristics such as are indicated in figure 1.

Preliminary work on the behavior of the fractions when vulcanized was carried out with a compound containing tetramethylthiuram disulphide, a rapid accelerator of vulcanization. A small quantity of compound containing each fraction was mixed on a laboratory mill and vulcanized in the form of rings. Tests of the vulcanized soluble fraction indicated a modulus, at 500 percent elongation, of 500 lb/in.^{2}. The modulus of the vulcanized insoluble fraction at the same elongation was 250 lb/in.^{2}. The insoluble (gel) fraction produced a much stiffer compound than the soluble (sol) fraction.

It appeared desirable to use a slow accelerator of vulcanization to accentuate any differences in the fractions through the greater diver-

gences of the stress-strain properties. Triphenylguanidine was chosen, and the following compound was used:

Ingredients	Parts by weight
Rubber	100
Sulphur	3
Zinc oxide	5
Stearic acid	1
Triphenylguanidine	2
Phenyl-β-naphthylamine	1

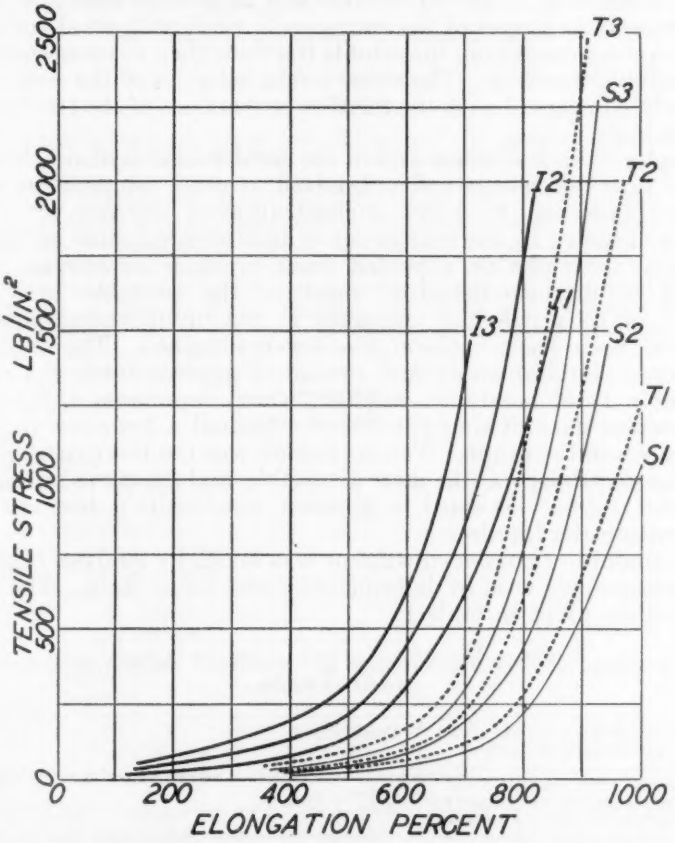

FIGURE 1.—*Stress-strain curves of soluble* (*S*), *insoluble* (*I*), *and total* (*T*) *rubbers.* Numerals 1, 2, and 3 indicate short, medium, and long cures, respectively.

Three lots were prepared, one containing the soluble fraction, the second the insoluble or gel fraction, and the third for comparison contained total rubber hydrocarbon. The total hydrocarbon was purified by the method [6] which has been described, but was not separated into fractions.

The compounds were mixed in lots of about 50 grams each by careful manipulation on a small laboratory mill. While mixing, it was quite evident that a difference existed between the two fractions. The insoluble or gel fraction as distinguished from the other rubbers was

[6] See footnote 1.

difficult to "break down" or plasticize on the mill and the resulting compound retained a gristle-like character. Compounds were vulcanized in sheets 2 by 4 inches and about 0.040 inch thick, from which dumbbell specimens were cut out for test purposes. Three periods of vulcanization were used; these were 50, 70, and 100 minutes, respectively, at 142° C. Stress-strain results obtained with each compound are shown in figure 1.

At each period of vulcanization the compound containing the soluble fraction is more extensible than that containing the insoluble, and the total hydrocarbon has an intermediate position. As the total hydrocarbon consists of 75 percent soluble and 25 percent insoluble rubber, the stress-strain curves of the compounds made with total rubber are closer to those containing the soluble fractions than to those containing the insoluble fractions. The stress-strain behavior of the total rubber is therefore in accord with the relative proportions of the two fractions present in it.

Samples of each fraction and of the total rubber hydrocarbon were pressed into thin sheets and vulcanized at room temperature by the Peachey [7] process, in which vulcanization is effected by nascent sulphur obtained by the interaction of hydrogen sulphide and sulphur dioxide. As might be expected from previous experience, it was difficult to obtain satisfactory sheets of the insoluble (gel) rubber because of its gristle-like character in the unvulcanized condition. However, some fairly uniform sheets were obtained. The sheets were vulcanized simultaneously and contained approximately 0.4 percent (see table 1) of combined sulphur, which represents a light cure. Stress-strain data of ring specimens exhibited a behavior similar to that shown in the graph. The gel rubber was the less extensible fraction, the sol rubber was the more extensible, and the curve representing the total rubber occupied a position intermediate between those representing the fractions.

The amount of combined sulphur was found by analysis in samples of all compounds used in determining stress-strain data. The results obtained are given in table 1.

TABLE 1.—*Results of the determination of "combined" sulphur in samples of the vulcanized rubbers*

Percentage of S in the vulcanized rubbers prepared from—			Conditions of curing		Accelerators used in vulcanizing
Soluble rubber hydrocarbon	Insoluble rubber hydrocarbon	Total rubber hydrocarbon	Temperature	Time	
			° *C*	*Min.*	
1.94	1.84	1.96	126	30	Tetramethylthiuram disulphide.
1.35	1.34	1.21	142	50	Triphenylguanidine.
1.57	1.64	1.45	142	70	
1.91	2.04	1.81	142	100	
0.33	0.47	0.35	----------	----------	Vulcanized by Peachey process.

From these it appears that differences in the stress-strain behavior of the fractions and the total rubber were not caused by varying amounts of combined sulphur, but must have been due to differences in the rubber, which persisted through vulcanization.

WASHINGTON, August 21, 1934.

[7] Ind. Rubber J. **63**, 427 (1922).

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP721

Part of Journal of Research of the National Bureau of Standards, Volume 13, October 1934

HEAT OF COMBUSTION OF STANDARD SAMPLE BENZOIC ACID

By Ralph S. Jessup and Carleton B. Green

ABSTRACT

The bomb calorimeter in use at this Bureau and the methods of calibrating it and determining heats of combustion are briefly described. In an extensive series of observations, the value obtained for the heat of combustion of standard sample benzoic acid is 26,419 international joules per gram mass (weight corrected for air buoyancy) when the sample is burned at 25° C in oxygen under an initial pressure of 30 atmospheres absolute, in a bomb of constant volume, the mass of sample and the mass of water placed in the bomb each being 3 g per liter of bomb volume. This value is in agreement within 0.03 percent with the values deduced from the data obtained in 1928 by Roth, Doepke, and Banse and by Jaeger and von Steinwehr, but is lower by 0.07 and 0.06 percent respectively than the values deduced from the data obtained by Fischer and Wrede in 1909 and by Dickinson in 1914.

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I. INTRODUCTION

The heat of combustion of benzoic acid, which is used as a standard substance for the calibration of bomb calorimeters, has been determined with a high degree of precision by a number of observers [1] [2] [3] [4] [5] in the last 25 years.

On account of possible differences in purity of lots of benzoic acid prepared at different times, it is desirable to determine the heat of combustion of each lot of the material used for the standard sample. A new determination is particularly desirable in view of the fact, recently pointed out by Washburn,[6] that the results obtained in bomb

[1] Fischer and Wrede, Z.phys.Chem. **69**,218(1909).
[2] Wrede, Z.phys.Chem. **75**,81(1910).
[3] Dickinson, Bul.BS **11**,189(1914) S230.
[4] Roth, Doepke, and Banse, Z.phys.Chem. **133**,431(1928).
[5] Jaeger and von Steinwehr, Z.phys.Chem. **135**,305(1928).
[6] BS J.Research **10**,525(1933); RP546.

calorimetric determinations depends to some extent on such variables as initial oxygen pressure, amount of water placed in the bomb, mass of the charge burned, and volume of the bomb.

This paper describes the measurements, made at the National Bureau of Standards during the last 2 years, of the heat of combustion of 2 lots of benzoic acid, designated as standard samples 39d and 39e.

II. METHOD AND APPARATUS

1. METHOD

The method is practically the same as that used by Dickinson.[7] The electrical energy equivalent of a calorimetric system, consisting of calorimeter, bomb, oxygen, electric heater, thermometer, and a weighed amount of water, is determined by supplying a measured quantity of energy electrically and observing the resultant rise in temperature. The rise in temperature of the system due to the combustion of a known mass of a given material is then a measure of the heat of combustion of the material under the conditions of the bomb process.

2. APPARATUS

The calorimetric equipment is practically the same as that used by Dickinson, and is described in detail in the reference cited. A schematic diagram of the calorimeter is shown in figure 1.

The equipment used in the present work differs from that used by Dickinson in the following respects:

1. The temperature of the jacket was maintained constant within 0.005° C by means of an oscillating-contact type of thermoregulator, which has been described by Sligh.[8]

2. The temperature of the calorimeter was measured by means of a platinum resistance thermometer of the calorimetric type, previously described by Sligh.[9] It was calibrated by measuring its resistance at the ice and steam points and by comparison at 50° C with a strain-free platinum resistance thermometer which had been calibrated in accordance with the procedure [10] for realizing the international temperature scale. The constants of the thermometer are given in table 1, where R_0 represents the resistance at 0° C, F the change in resistance between 0 and 100° C, and δ the other constant in the Callendar formula:

$$\theta=\frac{R_\theta-R_0}{F}100+\delta\left(\frac{\theta}{100}\right)\left(\frac{\theta}{100}-1\right)$$

TABLE 1.—*Constants of resistance thermometer*

Date	R_0	F	δ
August 20, 1920	25.6896	10.0563	1.474
June 30, 1926	25.6905	10.0569	1.455
August 28, 1931	25.6918	10.0565	.....
September 26, 1933	25.6920	10.0567	1.462

[7] Bul. BS 11,189(1914);S230.
[8] J. Am. Chem. Soc. 42,60(1920).
[9] BS Sci. Pap. 17,49(1921);S407.
[10] BS J.Research,1,635(1928);RP22.

The changes in the constants given in table 1 result in a change of only about 0.01 percent in the slope of the resistance-temperature curve at 30° C. The change during the course of the present work is apparently much less than this, although unfortunately, the δ was not determined in 1931. For calorimetric measurements of heats of combustion the constants of the thermometer need not be accurately known. In the limiting case where the electrical-energy experiments and the combustion experiments are made over exactly the same tem-

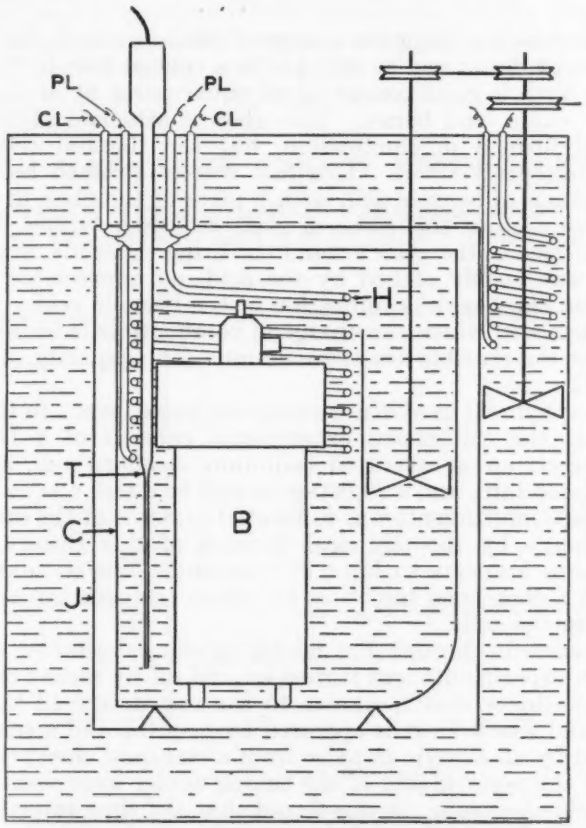

FIGURE 1.—*Schematic diagram of calorimeter.*

B, bomb; H, heater; C, calorimeter vessel; T, resistance thermometer; J, jacket; PL, potential leads; CL, current leads.

perature interval the relation between resistance of the thermometer and temperature is of no consequence whatever.

The Wheatstone bridge used in connection with the resistance thermometer has been described by Waidner, Dickinson, Mueller, and Harper.[11] The bridge was calibrated in terms of the international ohm by the method described in the reference cited.

3. The bomb is of the Parr type and is made of "illium", a corrosion-resisting alloy. This bomb has been used for several hundred combustions, but shows no signs of oxidation or corrosion. The cover

[11] Bul. BS 11,571(1914);S241.

of the bomb was originally provided with a check valve, and the joint between the cover and the bomb was made gas-tight by means of a rubber gasket. This cover was discarded and a new cover was made having a needle valve, the base of which is an integral part of the cover. A tongue on the cover fits into a groove 1 mm wide in the top of the bomb. A gold washer in the groove makes a gas-tight joint between the cover and the bomb. The bomb was originally supported by 3 pins about 3 mm in height. These were replaced by pins 12 mm high so as to permit freer circulation of water beneath the bomb.

The electrode for firing the charge of combustible in the bomb is a conical pin of illium and is sealed into a conical hole in the cover of the bomb with a glass consisting of equal parts by weight of soda glass, zinc oxide, and borax. This glass is attacked slightly by the nitric acid formed in combustion, but the thermal effect of this action is negligibly small. This fact was established by a number of combustions of benzoic acid with a piece of the glass in the bomb. The surface area of this piece of glass was many times that of the exposed surface of the glass around the firing electrode, and although the glass was visibly etched by the acid, no appreciable effect was observed on the heat of combustion of the benzoic acid.

The crucible in which the charge of combustible is burned and the support for the crucible are of platinum. The capacity of the bomb is 377 cm^3.

4. The equipment used in measuring the power input to the calorimeter during the calibration experiments consists of a Diesselhorst potentiometer, an unsaturated cadmium standard cell, a 0.01-ohm resistance standard, and a 20,000-ohm volt box with a ratio of 1,000:1. Each of these instruments was calibrated in terms of the international electrical units by the electrical division of this Bureau, and was certified to be accurate within 0.005 percent. The standard cell was inclosed in a cork-lined box so as to reduce temperature changes and gradients in the cell.

5. The current through the heater in the calorimeter during the calibration experiments was turned on and off by means of a double-pole double-throw switch similar to the one described by Osborne, Stimson, and Fiock.[12] It is operated by a spring and a release which is actuated by an electric impulse from a standard clock.

Tests of the performance of the timing device were made by means of a tape chronograph. It was found that the time interval between the receipt of the impulse and the operation of the switch varied from 0.01 to 0.03 second depending on the adjustment of the timing device. However the difference in the time of turning on and the time of turning off of the current was independent of the adjustment within the accuracy of the measurements with the chronograph. The average time required to turn on the current was greater than the average time required to turn it off by 0.007 second. For a given adjustment of the timing device, the greatest error that could have been introduced by combining the shortest observed time of turning on with the longest observed time of turning off of the current, or vice versa, was 0.018 second, or just 0.01 percent of the shortest heating time used in any of the calibration experiments.

[12] BS J.Research **5**, 429(1930); RP209.

6. The balance used for weighing the water of the calorimeter is sensitive to about 0.1 g, or about 0.003 percent of the total weight of calorimeter, heater, and water. The accuracy of the weights used with this balance is not important, since they were used only to obtain the same quantity of water in each experiment, and the same weights were always used.

The balance used for weighing the samples of benzoic acid is sensitive to a few hundredths of a milligram. The balance was tested, and the arms were found to be equal within the accuracy of the measurements (about 0.003 percent). The weights used with this balance were calibrated by the weights and measures division of this Bureau, and the corrections found were applied in calculating the weights of the samples of benzoic acid.

III. ELECTRICAL ENERGY EXPERIMENTS

The electrical energy equivalent of the calorimeter was determined by supplying a measured quantity of energy electrically and observing

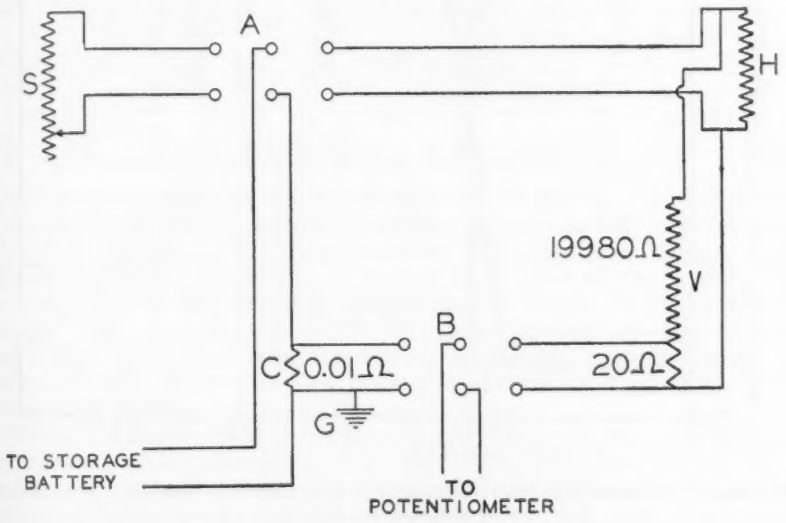

FIGURE 2.—*Power-measuring circuit.*

S, stabilizing resistance; A, switch operated by timing device; H, heater in calorimeter; C, 0.01 ohm resistance; G, ground; V, volt box.

the temperature rise produced. A diagram of the power-measuring circuits is shown in figure 2. Current from a storage battery flows through either the stabilizing resistance, S, or the heater, H, in the calorimeter, depending on which way the switch, A, is thrown. The resistance, S, is adjusted to approximate equality with H so that when the switch, A, is thrown only a small change is made in the current drawn from the storage battery. The power circuit was grounded at G (fig. 2) to metal plates placed under the calorimeter, bridge, potentiometer, and galvanometers.

The power input to the calorimeter is measured by observing the potential drops across the heater and the 0.01 ohm resistance standard, C (fig. 2). Before and after each experiment a zero reading is made on

the potentiometer with the switch B (fig. 2) thrown as if to measure the potential drop across the 20 ohms of the volt box. This is to determine the magnitude of thermal emf's in the galvanometer circuit.

The relation between resistance of the thermometer and time in a heat-capacity determination is represented by the curve shown in figure 3, where AB, BC, and CD represent the relations between resistance and time for the initial, middle, and final periods, respectively.

Correction for heat transfer between calorimeter and jacket was made by Dickinson's [13] method. This consists in extrapolating the resistance-time curves of the initial and final periods to a time, t_M, so chosen that the areas BEF and FGC (fig. 3) are equal. The difference in the temperatures corresponding to the points E and G (fig. 3) is then the temperature rise of the calorimeter corrected for heat transfer

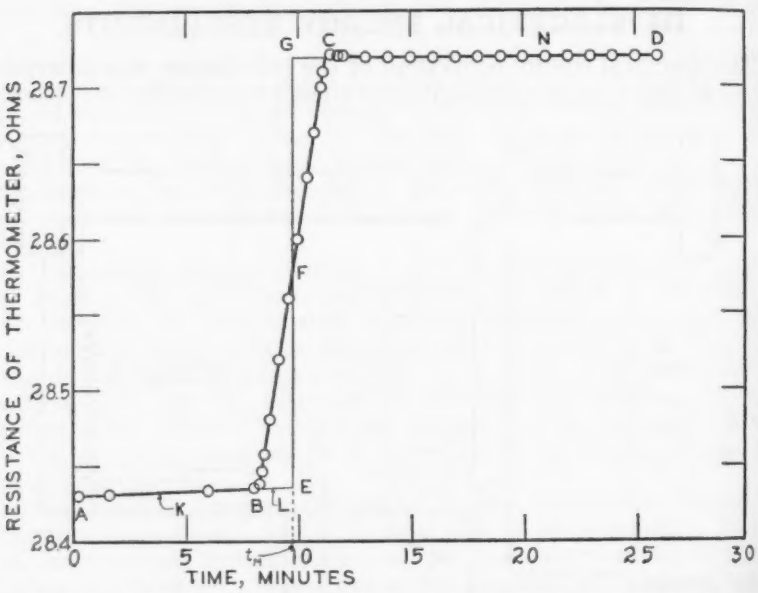

FIGURE 3.—*Relation between resistance of thermometer and time in a heat-capacity determination.*

between the calorimeter and its surroundings, and also for heat of stirring.

This method of correcting for heat transfer is based on Newton's law of cooling in the form:

$$\frac{dR}{dt} = -\alpha(R-R')$$

where R is the resistance of the thermometer and R' its resistance at the convergence temperature of the calorimeter.

To determine whether this law is valid over the temperature range covered in the calibration and combustion experiments, measurements were made of $\frac{\Delta R}{\Delta t}$ for various calorimeter temperatures while the tem-

[13] Bul. BS 11, 189(1914);S230.

perature of the jacket was kept constant. The measured values of $\frac{\Delta R}{\Delta t}$ are compared in table 2 with the values calculated from the equation

$$\frac{\Delta R}{\Delta t} = -0.00004058\ (R - 28.7259)$$

where R is the average resistance of the thermometer during the time interval Δt.

TABLE 2.—*Comparison of observed and calculated values of* $\frac{\Delta R}{\Delta t}$

R	$\frac{\Delta R}{\Delta t} \times 10^3_{obs.}$	$\frac{\Delta R}{\Delta t} \times 10^3_{calc.}$	$O-C$
ohms	*ohms/sec*	*ohms/sec*	*ohms/sec*
27.9447	3161	3170	−9
28.0657	2684	2679	+5
28.2098	2101	2094	+7
28.3317	1599	1600	−1
28.4498	1121	1120	+1
28.5507	712	711	+1
28.6556	280	285	−5
28.7648	−207	−158	−49
28.7639	−168	−154	−14
28.8818	−669	−633	−36
28.8778	−651	−616	−35

It will be seen from this table that for positive values of $\frac{\Delta R}{\Delta t}$, that is for the temperaure of the calorimeter below that of the jacket, the agreement between observed and calculated values is very satisfactory. The large differences between observed and calculated values, when the calorimeter temperature is higher than that of the jacket, are probably due to the variable evaporation of water from the calorimeter. The procedure in both the heat-capacity determinations and in the combustion experiments was such that the temperature of the calorimeter never exceeded that of the jacket by more than a few tenths of a degree.

Figure 4 is a sample of the records taken during an electrical-energy experiment. The observations in the columns headed "resistance" and "time" are the observed resistances of the thermometer and the corresponding times in minutes and seconds as read on a stop-watch. The items in the column headed "dif." are the differences between successive times of observation in the initial period, and differences between successive readings of resistance in the final period.

The items, dR, in the columns headed (r_1) and (r_2) are the total changes in resistance of the thermometer during the initial and final periods respectively, and the items dt are the corresponding elapsed times. The items, $\frac{dR}{dt}$, are the average time rates of change of resistance of the thermometer during the initial and final periods, respectively. The item, "cor.", in the column headed (r_1) is a correction which is applied to $\frac{dR}{dt}$ to take account of the fact that the resistance-time curve of the initial period is not quite linear. The

sum of $\frac{dR}{dt}$ and cor. is equal to r_1[r in the column headed (r_1)], which is the value of $\frac{dR}{dt}$ corresponding to the thermometer resistance repre-

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
WASHINGTON

Observers R.S.J. & C.B.G. Date 6-14-32
Computed by C.B.G. Expt. No. 11

ENERGY EQUIVALENT RECORD

					(r_1)	(r_2)	TIME	DIF.	RESISTANCE	NOTES
t_a	8:00		dR/	0.0054	0.00006	0:11	16	28.4300	Bridge BS. 7481
t_n	9:43		dt	469"	600"	27	19	02	Temp. 33.0°
dt	1:43=103"		$\frac{dR}{dt}$	0.04 1152	0.06 10	46	17	04	Calib. of 8-28-31
r_1	0.04 1139		Cor.	-13	0	1:03	17	06	Ratio 100
$r_1 dt$	0.00117		r	0.04 1139	0.06 10	20	15	08	Therm. Pt-11
R_1	28.43540		α	0.04 398		35		10	5 milliamps.
R_1cor.	28.43657		R_n	28.7221					
						5:58	15	28.4340	
Potentiometer No.	6000	Cell No.	56550			6:13	18	42	
Volt Box No.	245	Std. Res. No.	963			31	19	44	
Temp.	26.6°	Temp.	26.7°			50	16	46	
	45.847			4.6070		7:06	17	48	
	47			70		23	18	50	
	47			69		41	19	52	
				69		8:00		54	
Mean	45.8470	Mean		4.60695		14		28.4376	
Pot. Cor.	-20	Pot. Cor.		-20		21		.4464	
Vlth. fctr.	-28	Res. Std.		-115		28		.4574	
Zero corr.	00	Vlt. bx. cur.		-229		41		.48	
		Zero corr.		00		9:06		.52	
Volts	45.8422	Amperes		4.60331		32		.56	
Resistance	9.9585	Power		211.026		57		.60	
						10:22		.64	
on 8:00	Time 179.993	Energy 37983.2				41		.67	
off 11:00						11:00		.70	
t_a	16:00	Calorimeter No.	B			06		.71	
t_n	9:43	Bomb B.S. 30742				25		.7216	
dt	6:17 = 377"	1 cm^3 water in bomb				45		.7208	
r_2	0.06 10	Oxygen pressure, 30 At.				12:00		.7203	
$r_2 dt$	0.00004								
R_2	28.71954	Wt. of calorimeter,				13	-10	28.71966	
R_2Cor.	28.71950	water, and heater				14	-3	56	
R_1Cor.	28.43657	3630 grams				15	+1	53	
diff	0.28293					16	0	54	
Bdg	-1					17	0	54	
						18	+1	54	
dR	0.28292					19	+1	55	
K	9.8817	ROOM TEMP THERM.	30481	JACKET THERM.	Pt-11	20	+1	56	
dt	2.7957	Time	Temp.	Time	Temp.	21	+2	57	
Equiv.	13586.1	5	26.8	0	25.827	22	0	59	
Mn. Tmp.	26.40°	15	26.9	27	.825	23	+1	59	
						24	0	60	
						25	0	60	
						26		60	

FIGURE 4.—*Sample of records made in an electrical energy equivalent determination*

sented by the point L in figure 3, where L is midway between B and E. The correction, cor., is given by (see fig. 3):

$$\text{cor.} = -\alpha\,(R_L - R_K)$$

where

$$\alpha = -\frac{d}{dR}\left(\frac{dR}{dt}\right) = -\frac{\left(\frac{dR}{dt}\right)_N - \left(\frac{dR}{dt}\right)_K}{R_N - R_K}$$

R_K=average resistance in initial period
R_N=average resistance in final period.
The corresponding value of the correction to the rate in the final period is usually negligible.

The item, t_R, at the extreme left at top of figure 4 is the time of the last observation of resistance in the initial period, t_M has already been defined, dt is $(t_M - t_R)$, r_1 is the value of r from the column headed (r_1), R_1 is the final reading of resistance in the initial period, and R_1 cor. the sum of R_1 and $r_1\ dt$. R_1 cor. is therefore the value of resistance obtained by extrapolating the initial resistance-time curve to the time, t_M.

The corresponding items for the final period are given at the left of figure 4 and a little below the middle of the page. The item, "diff.", below R_1 cor. is (R_2 cor.$-R_1$ cor.). The item, "Bdg." is the difference in the corrections to the bridge for the initial and final readings, and dR is the corrected change in resistance of the thermometer, $(R_G - R_E)$ in figure 3. The item, K, is the value of $\frac{d\theta}{dR}$ corresponding to the mean of R_1 cor. and R_2 cor. (where θ is temperature), and is obtained by differentiating the Callendar equation as described by Dickinson and Mueller.[14] The item $d\theta$ is the corrected temperature rise corresponding to the resistance change dR.

The recorded values of voltage near the middle of figure 4 are the readings of potential drop across 20 ohms of the volt box multiplied by 1,000, the nominal value of the volt-box ratio. The recorded values of current are the readings of potential drop across the resistance standard divided by 0.01, the nominal resistance of the standard. The corrections to current and voltage, and other items of the figure are self-explanatory.

The results of the electrical-energy experiments are listed in table 3. Conditions were varied in order to detect possible systematic errors. Voltage was varied from 28 to 55, time of heating from 3 to 7 minutes, and temperature rise from 1.7 to 4.8° C. The final temperature in each experiment was within 0.1 or 0.2° of 30.0° C, so that the mean temperatures varied from 27.6 to 29.2°. The results were not corrected to a common mean temperature since the rate of change with temperature of the electrical energy equivalent of the system is negligibly small at this temperature.

[14] Bul. BS 9,483(1913);S200.

TABLE 3.—*Results of electrical energy experiments*

[First Series, Dec. 14 to 18, 1931]

Experiment number	Potential drop across heater E	Current through heater E/R	Time of heating t	Energy supplied to cal. $Q=(E^2/R)t$	Temperature rise (corrected) $\Delta\theta$	Observed electrical energy equivalent $Q/\Delta\theta$	Weight of calorimeter +water+ heater W	Electrical energy equivalent for W=3,630 g	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	Int. volts	*Int. amp.*	*Seconds*	*Int. joules*	*°C*	*Int. j/°C*	*g*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*
1	55.277$_9$	5.5535$_4$	179.99$_3$	55255.7	4.0555$_1$	13624.$_2$	3640.0	13583.$_0$	−1.0	13584.$_0$	−3.2
2	55.257$_5$	5.5513$_4$	179.99$_3$	55213.4	4.0521$_1$	13625.$_2$	3640.0	13584.$_0$	0.0		
3	55.237$_2$	5.5493$_4$	179.99$_3$	55173.3	4.0488$_5$	13626.$_9$	3640.0	13585.$_1$	+1.0		
5	27.827$_6$	2.7922$_8$	419.99$_3$	32634.$_3$	2.4011$_9$	13590.$_9$	3630.0	13590.$_9$	+2.1		
6	27.745$_9$	2.7841$_1$	419.99$_3$	32443.$_5$	2.3876$_1$	13588.$_3$	3630.0	13588.$_3$	−0.5		
7	27.760$_3$	2.7855$_8$	419.99$_3$	32477.$_4$	2.3900$_6$	13588.$_5$	3630.0	13588.$_5$	−0.3		
8	27.756$_8$	2.7851$_7$	419.99$_3$	32468.$_2$	2.3890$_9$	13590.$_3$	3630.0	13590.$_3$	+1.4		
9	27.751$_0$	2.7846$_3$	419.99$_3$	32455.$_5$	2.3888$_5$	13586.$_2$	3630.0	13586.$_2$	−2.6	13590.$_0$	+2.8
16	28.320$_7$	2.8418$_0$	419.99$_3$	33801.$_8$	2.4866$_7$	13593.$_2$	3630.0	13593.$_2$	+2.1		
17	28.318$_3$	2.8416$_0$	419.99$_3$	33796.$_5$	2.4870$_3$	13589.$_1$	3630.0	13589.$_1$	−2.0		
18	28.313$_9$	2.8411$_8$	419.99$_3$	33786.$_2$	2.4859$_9$	13590.$_6$	3630.0	13590.$_6$	−0.5		
19	28.309$_2$	2.8407$_2$	419.99$_3$	33775.$_2$	2.4847$_3$	13593.$_1$	3630.0	13593.$_1$	+2.0		
20	28.302$_3$	2.8400$_2$	419.99$_3$	33758.$_6$	2.4841$_4$	13589.$_7$	3630.0	13589.$_7$	−1.4		
10	46.038$_4$	4.6230$_6$	179.99$_3$	38309.$_4$	2.8184$_5$	13592.$_4$	3630.0	13592.$_4$	+3.6		
11	45.930$_0$	4.6121$_3$	179.99$_3$	38128.$_8$	2.8059$_7$	13588.$_8$	3630.0	13588.$_8$	−0.5		
12	45.886$_7$	4.6077$_5$	179.99$_3$	38056.$_7$	2.8006$_4$	13588.$_6$	3630.0	13588.$_6$	−0.2	13588.$_8$	+1.6
13	45.837$_7$	4.6029$_8$	179.99$_3$	37976.$_6$	2.7949$_4$	13587.$_6$	3630.0	13587.$_6$	−1.2		
14	45.792$_0$	4.5981$_8$	179.99$_3$	37899.$_3$	2.7892$_1$	13587.$_8$	3630.0	13587.$_8$	−1.9		
15	45.743$_7$	4.5934$_0$	179.99$_3$	37820.$_0$	2.7833$_5$	13587.$_9$	3630.0	13587.$_9$	−0.9		
Mean of first series								13588.$_8$			

[Second Series, May 16 to 20, 1932]

(wt of cal.+heater+water=3630.0 g in all experiments)

1	46.3955	4.6589$_4$	179.99$_3$	38906.$_5$	2.8623$_4$			13592.$_6$	+3.1		
2	46.3669	4.6550$_7$	179.99$_3$	38857.$_4$	2.8589$_3$			13591.$_6$	+2.1	13589.$_5$	+2.3
11	46.7739	4.6970$_7$	180.99$_3$	39764.$_2$	2.9267$_3$			13586.$_5$	−3.0		
12	46.7335	4.6930$_0$	179.99$_3$	39476.$_1$	2.9063$_6$			13587.$_3$	−2.2		
3	46.3272	4.6520$_2$	299.99$_3$	64653.$_0$	4.7584$_8$			13586.$_9$	+2.0		
4	46.2904	4.6485$_3$	299.99$_3$	64550.$_4$	4.7513$_5$			13585.$_7$	+0.8		
13	46.6342	4.6830$_0$	299.99$_3$	65514.$_9$	4.8224$_3$			13585.$_4$	+0.5	13584.$_9$	−2.3
14	46.5806	4.6776$_0$	299.99$_3$	65364.$_1$	4.8124$_6$			13582.$_3$	−1.6		
15	46.5073	4.6702$_7$	304.99$_3$	66245.$_7$	4.8766$_7$			13584.$_2$	−0.7		
16	46.4299	4.6624$_1$	299.99$_3$	64940.$_1$	4.7803$_6$			13584.$_8$	−0.1		
5	55.5570	5.5813$_8$	179.99$_3$	55813.$_1$	4.1088$_6$			13583.$_6$	+0.5		
6	55.4837	5.5739$_5$	179.99$_3$	55665.$_0$	4.0986$_0$			13581.$_5$	−1.6		
7	55.3717	5.5627$_5$	179.99$_3$	55441.$_3$	4.0822$_5$			13581.$_1$	−2.0	13583.$_1$	−4.1
8	55.3306	5.5586$_0$	179.99$_3$	55357.$_2$	4.0756$_2$			13582.$_5$	−0.6		
9	55.2957	5.5551$_3$	179.99$_3$	55289.$_3$	4.0704$_2$			13583.$_2$	+0.1		
10	55.2767	5.5532$_5$	179.99$_3$	55251.$_6$	4.0686$_9$			13586.$_4$	+3.2		
17	36.8898	3.7027$_3$	359.99$_3$	49171.$_2$	3.6186$_0$			13588.$_5$	+4.2		
18	36.8853	3.7024$_3$	359.99$_3$	49162.$_5$	3.6197$_9$			13581.$_6$	−2.7		
19	36.9425	3.7081$_7$	359.99$_3$	49315.$_5$	3.6309$_0$			13582.$_2$	−2.1	13584.$_3$	−2.9
20	36.8946	3.7032$_9$	359.99$_3$	49185.$_5$	3.6211$_7$			13582.$_8$	−1.5		
21	36.8715	3.7010$_5$	359.99$_3$	49125.$_6$	3.6159$_7$			13585.$_7$	+1.4		
22	36.8633	3.7001$_9$	359.99$_3$	49103.$_5$	3.6144$_8$			13585.$_2$	+0.9		
23	27.9875	2.8084$_2$	299.99$_3$	23579.$_6$	1.7349$_4$			13591.$_0$	+4.8		
24	27.9735	2.8070$_6$	299.99$_3$	23555.$_8$	1.7343$_0$			13582.$_3$	−3.9		
25	27.9619	2.8058$_8$	299.99$_3$	23536.$_3$	1.7321$_0$			13588.$_3$	+2.1	13586.$_2$	−1.0
26	27.9477	2.8044$_6$	299.99$_3$	23512.$_4$	1.7304$_7$			13587.$_3$	+1.1		
27	27.9373	2.8033$_5$	299.99$_3$	23494.$_9$	1.7296$_0$			13584.$_0$	−2.2		
28	27.9274	2.8024$_0$	299.99$_3$	23478.$_8$	1.7284$_9$			13583.$_2$	−3.0		
Mean of second series								13585.$_3$			

TABLE 3.—*Results of electrical energy experiments*—Continued

[Third Series, June 1932]

Experiment number	Potential drop across heater E	Current through heater E/R	Time of heating t	Energy supplied to cal. $Q=(E^2/R)t$	Temperature rise (corrected) $\Delta\theta$	Observed electrical energy equivalent $Q/\Delta\theta$	Weight of calorimeter + water + heater W	Electrical energy equivalent for $W=3{,}630$ g	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	Int. volts	*Int. amp.*	*Seconds*	*Int. joules*	*°C*	*Int. j/°C*	*g*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*
1	55.270$_7$	5.5525$_5$	179.99$_3$	55239.$_5$	4.065$_7$			13586.$_7$	−1.3		
2	55.161$_4$	5.5418$_2$	179.99$_3$	55022.$_8$	4.050$_0$			13585.$_9$	−2.1		
3	55.120$_0$	5.5375$_8$	179.99$_3$	54939.$_6$	4.043$_4$			13587.$_5$	−0.5	13588.$_0$	+0.8
4	55.088$_0$	5.5342$_7$	179.99$_3$	54874.$_8$	4.038$_1$			13589.$_3$	+1.3		
5	55.069$_0$	5.5325$_2$	179.99$_3$	54838.$_6$	4.035$_4$			13589.$_4$	+1.4		
6	55.070$_7$	5.5325$_7$	179.99$_3$	54840.$_8$	4.035$_6$			13589.$_3$	+1.3		
7	45.923$_2$	4.6114$_2$	179.99$_3$	38117.$_3$	2.805$_5$			13586.$_7$	−0.7		
8	45.907$_2$	4.6098$_5$	179.99$_3$	38091.$_1$	2.803$_6$			13589.$_4$	+2.0		
9	45.885$_5$	4.6077$_1$	179.99$_3$	38055.$_4$	2.800$_8$			13587.$_4$	0.0	13587.$_4$	+0.2
10	45.863$_9$	4.6054$_6$	179.99$_3$	38018.$_9$	2.798$_1$			13587.$_4$	0.0		
11	45.842$_2$	4.6033$_1$	179.99$_3$	37983.$_2$	2.795$_8$			13586.$_1$	−1.3		
12	45.824$_2$	4.6015$_1$	179.99$_3$	37953.$_4$	2.793$_2$			13587.$_8$	+0.4		
13	46.442$_3$	4.6637$_2$	299.99$_3$	64976.$_5$	4.781$_8$			13588.$_3$	+1.3		
14	46.415$_8$	4.6610$_6$	299.99$_3$	64902.$_5$	4.777$_4$			13585.$_3$	−1.8		
15	46.367$_2$	4.6562$_6$	300.99$_3$	64983.$_7$	4.782$_7$			13587.$_3$	+0.2	13587.$_1$	−0.1
16	46.321$_3$	4.6516$_0$	299.99$_3$	64638.$_9$	4.757$_1$			13587.$_9$	+0.8		
17	46.285$_4$	4.6479$_4$	299.99$_3$	64538.$_4$	4.750$_0$			13587.$_0$	−0.1		
18	46.248$_6$	4.6442$_7$	299.99$_3$	64435.$_8$	4.742$_6$			13586.$_6$	−0.5		
19	28.072$_4$	2.8169$_8$	299.99$_3$	23723.$_2$	1.746$_0$			13587.$_2$	−0.3		
20	28.058$_9$	2.8155$_9$	299.99$_3$	23700.$_1$	1.743$_9$			13590.$_3$	+2.8		
21	28.045$_3$	2.8142$_5$	299.99$_3$	23677.$_3$	1.742$_6$			13587.$_4$	−0.1	13587.$_5$	+0.3
22	28.034$_8$	2.8131$_8$	299.99$_3$	23659.$_5$	1.741$_3$			13587.$_3$	−0.2		
23	28.025$_1$	2.8122$_1$	299.99$_3$	23643.$_1$	1.740$_6$			13588.$_1$	+0.6		
24	28.014$_6$	2.8111$_6$	299.99$_3$	23625.$_5$	1.739$_1$			13584.$_9$	−2.6		
25	28.447$_5$	2.8546$_4$	419.99$_3$	34106.$_5$	2.510$_1$			13587.$_7$	−0.7		
26	28.341$_9$	2.8440$_0$	419.99$_3$	33853.$_2$	2.491$_3$			13588.$_6$	+0.2		
27	28.227$_8$	2.8325$_2$	419.99$_3$	33580.$_6$	2.471$_3$			13588.$_3$	−0.1	13588.$_4$	+1.2
28	28.161$_5$	2.8258$_5$	419.99$_3$	33423.$_1$	2.460$_0$			13586.$_5$	−1.9		
29	28.114$_3$	2.8211$_2$	419.99$_3$	33311.$_2$	2.451$_2$			13589.$_8$	+1.4		
30	28.079$_1$	2.8175$_9$	419.99$_3$	33227.$_9$	2.445$_1$			13589.$_6$	+1.2		
31	37.144$_9$	3.7284$_3$	359.99$_3$	49856.$_8$	3.668$_4$			13590.$_9$	+1.8		
32	37.105$_0$	3.7244$_8$	359.99$_3$	49749.$_9$	3.661$_0$			13589.$_1$	0.0		
33	37.072$_2$	3.7210$_6$	359.99$_3$	49660.$_2$	3.654$_2$			13589.$_5$	+0.4	13589.$_1$	+1.9
34	37.049$_9$	3.7189$_1$	359.99$_3$	49601.$_7$	3.650$_1$			13589.$_1$	0.0		
35	37.031$_1$	3.7170$_3$	359.99$_3$	49551.$_5$	3.647$_1$			13586.$_5$	−2.6		
36	37.009$_4$	3.7148$_5$	359.99$_3$	49493.$_4$	3.642$_6$			13589.$_6$	+0.5		
Mean of third series								13587.$_9$			
Mean of all observations								13587.$_2$			

The determinations were made with the calorimeter as nearly as possible in the same condition as in the combustion experiments. One cm^3 of water was placed in the bomb, which was filled with oxygen to a pressure of 30 atmospheres absolute. Hence for the combustion experiments at this pressure it is necessary to add only the heat capacity of the sample of combustible material to obtain the total electrical energy equivalent of the system.

In the first series of determinations 3 groups of measurements were made, in which the voltages impressed on the heater were approximately 55, 28, and 46 and the corresponding temperature changes of the calorimeter were 4.0, 2.4, and 2.8°, respectively. The means of the results obtained in the second and third groups (28 and 46 volts) are in agreement within less than 0.01 percent, while the results obtained in the first group are lower by 0.04 percent. It was noticed that if the results were plotted against the temperature rise of the calorimeter the points would lie very nearly on a straight line. Such an effect as this could not possibly be an actual change in the energy equivalent of the calorimeter with temperature rise, but might be the result of some pecularity of the thermometer, possibly arising from mechanical strain in the platinum wire.

In order to check the results of the first series of electrical energy experiments a second series was made, consisting of 5 groups of experiments, in which the temperature rise of the calorimeter was varied from 1.7 to 4.8°. It will be seen from table 3 that the results obtained in the second series of experiments for temperature rises of 2.9 and 4.1° are in agreement within 0.01 percent with the corresponding groups of the first series, and that the results obtained with a 3.6° temperature rise are intermediate between those obtained with temperature rises of 2.9 and 4.1°. These 3 groups of experiments therefore appear to confirm the apparent variation of energy equivalent with temperature rise observed in the first series of experiments. However, the results obtained with temperature rises of 1.7 and 4.8° do not confirm this apparent variation.

In order to determine whether the differences in the results obtained were due to erratic behavior of the thermometer, it was carefully compared over the temperature range 25 to 30° with a strain-free thermometer. It was found that when the resistances of the calorimetric thermometer at 10 temperatures in this range were plotted against the corresponding resistances of the strain-free thermometer, the points lay on a smooth curve with a maximum deviation of 0.00002_5 ohm ($.0002_5$°C) and an average deviation of 0.00001 ohm (.0001°C). These results suggested that the variations in the results of the electrical energy experiments were not caused by erratic behavior of the thermometer.

Following these experiments a third series of electrical energy experiments was made, using a different potentiometer and standard cell from those used in the first and second series, all other equipment being the same as in the first two series. This series consisted of six groups of experiments made under the same conditions as those of the second series. It will be seen from table 3 that the results were remarkably consistent, showing no sign of any variation of energy equivalent with temperature rise. It was concluded at the time that the variations observed in the first 2 series could be attrib-

uted to the potentiometer or standard cell used in these series. However, it was found in making heat of combustion measurements with different amounts of benzoic acid in the bomb, that the results in some cases were consistent with the apparent variation of the energy equivalent of the calorimeter with temperature rise observed in the first two series of calibration experiments, while others were consistent with a value for the energy equivalent independent of temperature rise. It was finally found that the indications of the thermometer depend to some extent on its previous history, and it is believed that this explains the differences in the results obtained in the various groups of experiments.

It was found, for example, that the apparent variation of energy equivalent of the calorimeter with temperature rise was somewhat greater if the thermometer was cooled to about 23° C before each experiment, than if it was heated to 33° C before each experiment. It was also found that the resistance of the thermometer at 30° C was greater by 0.0001_4 ohm (0.001_4 ° C) if it had been recently cooled to 23° than if it had been heated to 33°. This was shown by comparisons with a strain-free thermometer which was left in a constant-temperature bath throughout the comparisons, while the calorimetric thermometer was occasionally removed from the bath and cooled to 23° or heated to 33° C.

Although the results obtained under various conditions differ by more than had been expected, it is believed that by taking the mean of all the results of the calibration experiments as the electrical energy equivalent of the calorimeter, and the mean of the results of a large number of combustion experiments made under various conditions as the heat of combustion of benzoic acid, the effect of the differences is largely eliminated. The justification for this belief lies in the fact that the means of the results in the 3 series of calibration experiments are in good agreement with the mean of all the results.

The mean of these 3 series, and of all of the calibration experiments are as follows:

First series	$13588._6$ int. joules/° C
Second series	$13585._3$ int. joules/° C
Third series	$13587._9$ int. joules/° C
All experiments	$13587._2$ int. joules/° C

The means of the various series are within less than 0.015 percent of the mean of all experiments. The maximum deviation of the mean of a single group of experiments made under the same conditions, from the mean of all experiments is 0.030 percent.

IV. COMBUSTION EXPERIMENTS

1. MATERIALS

(a) BENZOIC ACID

Measurements were made on 2 lots of benzoic acid, designated as standard samples 39d and 39e. These samples were of a high degree of purity and uniformity, but were not entirely free from small amounts of impurity. Chemical data on the 2 samples are given in table 4.

TABLE 4.—*Chemical data on standard samples 39d and 39e of benzoic acid*

Sample number	Purity of dried or fused sample on basis of titration [1]	Sulphur	Chlorine	Nonvolatile matter at 600° C	Heavy metals	Insoluble in diluted NH_4OH (1+3)
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	
39d	99.98	0.001	0.001	0.003		
39e	99.99	0.001	0.001	0.002	0.0005	none

[1] Compared with HCl which was standardized by weighing AgCl.

Freezing point measurements were made on sample 39d by means of a platinum resistance thermometer, in accordance with the technic described by Mair.[15] The initial freezing point was found to be 122.-30_5° C, and the freezing range 0.095° C. The purity estimated on the basis of these data is 99.88 mole percent. No freezing point measurements were made on sample 39e.

As a further check on the purity of the material, measurements were made of the amounts of carbon dioxide formed in the combustion of known masses of sample 39d. The carbon dioxide formed was absorbed in "ascarite" and weighed in the manner described by Rossini.[16]

In table 5 are given the ratios of the masses of CO_2 found to those calculated on the assumption that the material is pure benzoic acid. The atomic weights used in calculating this table are O=16.000, H=1.0078, and C=12.000. There is some evidence which indicates that the atomic weight of carbon is somewhat higher than 12.000.[17] If 12.007 had been used in calculation of the data of table 5, the average value of the ratio CO_2 found/CO_2 calculated would have been 0.9998_3.

TABLE 5.—*Results of measurements of* CO_2 *formed in combustion of standard sample 39d*

Experiment number	$\frac{CO_2 \text{ found}}{CO_2 \text{ calculated}}$	Deviation from mean
1	0.9998_3	+0.00024
2	$.9994_4$	−.00015
3	$.9996_3$	+.00004
4	$.9994_5$	−.00014
Mean	$.9995_9$	±.00014

(b) OXYGEN

Commercial oxygen containing a small amount of nitrogen was used. Before being admitted to the bomb the oxygen was passed through a tube containing copper oxide heated to a temperature of about 750° C, in order to burn out any combustible impurities

[15] BS J.Research **9**, 457(1932); RP482.
[16] BS J.Research **6**, 37(1931); RP260.
[17] 1934 report of International Committee on Atomic Weights, J. Am. Chem. Soc. **56**, 753(1934).

which might be present. The use of oxygen purified in this way resulted in a value for the heat of combustion of benzoic acid which was lower by about 0.03 percent than the value obtained with unpurified oxygen.

2. EXPERIMENTAL PROCEDURE AND CALCULATION OF RESULTS

The samples of benzoic acid were compressed into briquets, and weighed in that form in the platinum crucible in which they were to be burned. One cm^3 of water was placed in the bomb to saturate the space with water vapor at the beginning of the experiment. In most experiments the air initially in the bomb was washed out by filling the bomb several times with oxygen to 3 or 4 atmospheres pressure, and then allowing the oxygen to escape until the pressure was reduced to 1 atmosphere. The experimental procedure in the combustion experiments was as nearly as possible the same as in the calibration experiments.

The charge was ignited by means of an electric fuse consisting of a 2 cm length of iron wire about 0.13 mm in diameter (no. 36 B. & S. gage). The iron wire was connected to platinum leads, 0.20 to 0.25 mm in diameter. The current for firing the charge was obtained from a toy transformer having a secondary voltage of 14.

The energy used in firing the charge, that is the heat developed in the combustion of the iron plus the electric energy used to ignite the wire, was determined in a series of blank experiments in which only the iron wire was burned. The results obtained in these experiments are given in table 6.

TABLE 6.—*Energy required to ignite charge*

Experiment number	Firing energy	Deviation from mean
	int. joules	*int. joules*
1	22.6	−0.4
2	22.6	−.4
3	25.1	+2.1
4	23.8	+0.8
5	20.9	−2.1
Mean	23.0	±1.6

In the combustion experiments, as in the calibration experiments, the observed temperature rise of the calorimeter was corrected for heat transfer between calorimeter and jacket, and heat of stirring by Dickinson's method. The heat produced by the combustion of a sample of benzoic acid was calculated by multiplying the corrected temperature rise by the electrical energy equivalent of the system. The total electrical energy equivalent of the system is given by

$$C=C_0+1.26m_s+0.34\ (p_{o_2}-30)$$

where m_s is the mass of the sample of benzoic acid, p_{o_2} is the initial oxygen pressure in the bomb in atmospheres, at 30° C, and C_0 is the observed electrical energy equivalent of the calorimeter, including the bomb, containing 1 gram of water and oxygen under a pressure of 30 atmospheres absolute at 30° C.

From the total quantity of heat, Q, produced in an experiment were subtracted the energy, q_1 (=23.0 joules), used to ignite the sample, and the energy, $-\Delta U_{HNO_3}$, of formation of the nitric acid produced in the combustion. The energy of formation of nitric acid in the reaction

$$\frac{1}{2}\,N_2(gas)+\frac{5}{4}\,O_2(gas)+\frac{1}{2}\,H_2O\ (liq.)=HNO_3(aq.)(30°C)$$

is taken as 63,000 joules, a figure which is based on data given in International Critical Tables, vol. 5, 179.

The observed heat of combustion of the sample of benzoic acid at the final temperature of the calorimeter is given by

$$-\Delta U_B=\frac{Q-q_1+\Delta U_{HNO_3}}{m_s}$$

where m_s is the mass of the sample, and $-\Delta U_B$ is the heat evolved in the combustion of unit mass of the sample under the conditions of the bomb process.

The experimental conditions were varied over a wide range in order to detect possible systematic errors. The mass of sample was varied from 0.7 to 2.0g, the corresponding temperature rise varying from 1.4 to 3.9° C, and the oxygen pressure was varied from 20 to 30 atmospheres.

There was no indication of unburned carbon remaining in the crucible after combustion. The gaseous products of combustion in a number of experiments were examined for carbon monoxide by the method described by Eiseman, Weaver, and Smith.[18] No carbon monoxide was found although the method is capable of detecting amounts as small as 0.001 to 0.003 percent of the total amount of gas in the bomb at the end of the experiments.

3. RESULTS.

The results obtained for standard samples 39d and 39e are given in tables 7 and 8, respectively. The observed values of heat of combustion have been reduced by the method given by Washburn [19] to the heat of combustion for standard initial conditions. The standard conditions chosen are:

Initial oxygen pressure=30 atmospheres absolute at 30° C;
Mass of sample=3 g per liter of bomb volume;
Volume of water placed in bomb=3 cm^3 per liter of bomb volume;
Temperature to which reaction is referred=30° C.

[18] BS J. Research 8,669(1932); RP446.
[19] BS J. Research, 10,525(1933); RP546.

TABLE 7.—*Measurements of heat of combustion of standard sample 39d*

[Oxygen not purified in experiments 1 to 6; oxygen purified in experiments 7 to 63]

Experiment number	Weight of sample in air vs. brass weights	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for iron wire and electric energy	Heat produced by combustion of benzoic acid	Observed heat of combustion	Reduction to standard initial conditions	Heat of combustion for standard initial conditions	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	g	*atm*	*int. joules*	*int. joules*	*int. joules*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*
1	1.5193$_7$	30.2	40,286.7	77.0	23.0	40,186.7	26,449.6	−1.0	26,448.6	+4.3		
2	1.4987$_7$	30.2	39,748.4	75.8	23.0	39,649.6	26,454.8	−0.9	26,453.9	+9.6		
3	1.5185$_8$	30.2	40,246.2	67.6	23.0	40,155.6	26,442.9	−1.0	26,441.9	−2.4	26444.3	+8.4
4	1.4674$_8$	30.2	38,894.0	72.3	23.0	38,798.7	26,439.0	−0.9	26,438.1	−6.2		
5	1.5121$_1$	30.2	40,085.9	72.8	23.0	39,990.1	26,446.6	−1.0	26,445.6	+1.7		
6	1.5869$_0$	30.2	42,055.0	76.3	23.0	41,955.7	26,438.8	−1.0	26,437.8	−6.5		
7	1.5905$_3$	30.5	42,422.1	85.5	23.0	42,313.6	26,603.5	−1.2	(26,602.3)			
8	1.7976$_1$	30.4	47,642.9	89.8	23.0	47,530.3	26,440.8	−1.3	26,439.5	+1.4		
9	1.5704$_4$	30.4	41,606.0	79.1	23.0	41,503.9	26,428.2	−1.1	26,427.1	−11.0		
10	1.6851$_7$	30.2	44,664.0	85.0	23.0	44,556.0	26,440.0	−1.0	26,439.0	+0.9		
11	1.5726$_2$	30.2	41,678.1	82.0	23.0	41,573.1	26,435.5	−0.7	26,434.8	−3.3		
12	1.5143$_0$	30.2	40,134.0	77.9	23.0	40,033.1	26,436.7	−0.9	26,435.8	−2.3		
13	1.2569$_2$	30.2	33,325.2	66.5	23.0	33,235.7	26,442.1	+0.1	26,442.2	+4.1		
14	1.4605$_2$	30.5	38,700.1	70.2	23.0	38,606.9	26,433.6	−0.9	26,432.7	−5.4		
15	1.6654$_7$	30.1	44,135.3	75.8	23.0	44,036.5	26,440.9	−1.2	26,439.7	+1.6		
16	1.6352$_3$	30.1	43,330.6	78.9	23.0	43,228.7	26,435.8	−1.1	26,434.7	−3.4		
17	1.4323$_6$	30.0	37,969.0	66.5	23.0	37,879.5	26,445.5	−0.6	26,444.9	+6.8	26438.1	+3.2
18	1.4452$_4$	30.1	38,257.5	19.9	23.0	38,214.4	26,441.5	−0.7	26,440.8	+2.7		
19	1.4493$_6$	30.1	38,355.7	19.2	23.0	38,313.5	26,434.8	−0.7	26,434.1	−4.0		
20	1.5080$_0$	30.1	39,919.1	15.5	23.0	39,880.6	26,445.9	−0.8	26,445.1	+7.0		
21	1.4692$_2$	30.1	38,883.8	15.5	23.0	38,845.3	26,439.4	−0.7	26,438.7	+0.6		
22	1.4921$_7$	30.1	39,498.0	14.9	23.0	39,460.1	26,444.7	−0.8	26,443.9	+5.8		
23	1.6444$_2$	30.1	43,514.4	15.5	23.0	43,475.9	26,438.4	−1.1	26,437.3	−0.8		
50 [a]	1.5385$_8$	32.5	40,722.9	17.6	23.0	40,682.3	26,441.4	−2.2	26,439.2	+1.1		
51 [a]	1.5208$_0$	32.5	40,255.4	16.9	23.0	40,215.5	26,443.6	−2.2	26,441.4	+3.3		
52 [a]	1.5081$_7$	32.5	39,910.2	17.6	23.0	39,869.6	26,435.7	−2.2	26,433.5	−4.6		
24	1.4566$_3$	22.2	38,583.5	57.8	23.0	38,502.7	26,432.7	+3.5	26,436.2	−0.9		
25	1.6082$_8$	22.2	42,590.8	65.4	23.0	42,502.4	26,427.2	+3.1	26,430.3	−6.8		
26	1.5638$_1$	22.2	42,419.7	59.8	23.0	41,336.9	26,433.4	+3.2	26,436.6	−0.5		
27	1.4620$_2$	22.2	38,707.2	48.0	23.0	38,636.2	26,426.6	+3.5	26,430.1	−7.0		
28	1.5375$_3$	22.7	40,717.5	52.0	23.0	40,642.5	26,433.6	+2.9	26,436.5	−0.6	26437.1	+2.2
29	1.4803$_9$	22.7	39,224.3	54.6	23.0	39,146.7	26,443.5	+3.1	26,446.6	+9.5		
30	1.5293$_4$	22.7	40,505.6	51.9	23.0	40,430.7	26,436.7	+3.0	26,439.7	+2.6		
31	1.5429$_8$	22.7	40,884.6	68.2	23.0	40,793.4	26,438.0	+3.0	26,441.0	+3.9		
32	1.5398$_5$	22.5	40,792.0	57.2	23.0	40,711.8	26,438.8	+3.1	26,441.9	+4.8		
33	1.6394$_0$	22.7	43,407.1	55.7	23.0	43,328.2	26,429.2	+2.8	26,432.0	−5.1		

34	1.0292$_4$	30.7	27227.$_7$	13.$_9$	23.$_0$	27190.$_8$	26418.$_3$	+0.2	26418.$_4$	−17.4		
35	1.2169$_3$	32.1	32212.$_0$	16.$_8$	23.$_0$	32172.$_2$	26437.$_2$	−1.1	26436.$_1$	+0.3		
36	.9927$_8$	32.3	26294.$_9$	13.$_2$	23.$_0$	26258.$_7$	26449.$_7$	−0.7	26449.$_0$	+13.2		
37	1.0494$_7$	32.3	27780.$_2$	15.$_3$	23.$_0$	27741.$_8$	26434.$_1$	−0.7	26433.$_4$	−2.4		
38	.9912$_7$	32.3	26252.$_7$	14.$_5$	23.$_0$	26215.$_2$	26446.$_1$	−0.7	26445.$_4$	+9.6		
39	1.0643$_2$	32.3	28175.$_8$	15.$_2$	23.$_0$	28137.$_5$	26437.$_1$	−0.8	26436.$_3$	+0.5		
40	.9746$_0$	32.3	25902.$_2$	13.$_2$	23.$_0$	25866.$_0$	26540.$_1$	−0.6	(26539.$_5$)	----------	26435.$_8$	+0.9
41	1.0302$_6$	30.5	27285.$_7$	16.$_5$	23.$_0$	27246.$_2$	26445.$_9$	+0.3	26446.$_2$	+10.4		
53	1.0291$_1$	32.3	27232.$_5$	13.$_0$	23.$_0$	27196.$_8$	26427.$_2$	−0.7	26426.$_5$	−9.3		
54	1.0036$_1$	32.3	26561.$_2$	12.$_4$	23.$_0$	26525.$_8$	26430.$_4$	−0.7	26429.$_7$	−6.1		
55	1.0457$_7$	32.3	27686.$_5$	11.$_1$	23.$_0$	27652.$_4$	26442.$_1$	−0.7	26441.$_4$	+5.6		
56	1.0326$_5$	32.3	27001.$_4$	13.$_0$	23.$_0$	26965.$_4$	26112.$_8$	−0.7	(26112.$_1$)	----------		
57	1.0002$_6$	32.3	26474.$_2$	12.$_4$	23.$_0$	26438.$_8$	26431.$_9$	−0.7	26431.$_2$	−4.6		
58 [b]	1.0301$_8$	32.3	27264.$_1$	11.$_7$	23.$_0$	27229.$_4$	26431.$_7$	−0.7	26431.$_0$	−5.0		
59 [b]	.9958$_8$	32.3	26363.$_5$	10.$_4$	23.$_0$	26330.$_1$	26439.$_6$	−0.7	26438.$_3$	+2.3		
60 [b]	1.0020$_3$	32.3	26517.$_0$	10.$_4$	23.$_0$	26483.$_6$	26429.$_9$	−0.7	26429.$_2$	−6.8		
61 [b]	.9697$_7$	32.3	25676.$_2$	10.$_4$	23.$_0$	25642.$_8$	26442.$_1$	−0.7	26441.$_4$	+5.4	26436.$_0$	+1.1
62 [b]	1.0022$_7$	32.2	26533.$_3$	10.$_4$	23.$_0$	26499.$_9$	26439.$_9$	−0.7	26439.$_2$	+3.2		
63 [b]	1.0107$_4$	32.1	26754.$_6$	10.$_4$	23.$_0$	26721.$_2$	26437.$_3$	−0.7	26436.$_6$	+0.6		
42	.9791$_2$	22.0	25904.$_8$	13.$_9$	23.$_0$	25867.$_9$	26419.$_4$	+4.9	26424.$_3$	−5.8		
43	.9917$_9$	21.9	26251.$_2$	15.$_2$	23.$_0$	26213.$_6$	26430.$_0$	+4.9	26434.$_9$	+4.8		
44	1.0012$_7$	21.9	26495.$_8$	13.$_9$	23.$_0$	26458.$_9$	26425.$_3$	+4.9	26430.$_2$	+0.1		
45	1.0102$_9$	21.9	26771.$_6$	44.$_2$	23.$_0$	26704.$_4$	26432.$_4$	+4.9	26437.$_3$	+7.2		
46	1.0318$_2$	22.5	27300.$_5$	13.$_2$	23.$_0$	27264.$_3$	26423.$_4$	+4.5	26427.$_4$	−2.2	26430.$_1$	−5.9
47	1.0149$_7$	22.5	26852.$_1$	14.$_5$	23.$_0$	26814.$_6$	26419.$_1$	+4.5	26423.$_6$	−6.5		
48	.9865$_2$	22.3	26104.$_7$	11.$_2$	23.$_0$	26070.$_5$	26426.$_8$	+4.7	26431.$_5$	+1.4		
49	.9849$_2$	21.3	26064.$_7$	14.$_5$	23.$_0$	26027.$_2$	26425.$_7$	+5.2	26430.$_9$	+0.8		
Mean of all observations on standard sample 39d except experiments 1 to 7, inclusive, 40, 56, and 58 to 63, inclusive									26436.$_0$			

[a] Fused samples.
[b] Large piece of low-melting-point glass in bomb.

TABLE 8.—*Measurements of heat of combustion of standard sample 39e*

MATERIAL DRIED AT 105° C

Experiment number	Wt. of sample in air vs. brass weights	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for iron wire and electric energy	Heat produced by combustion of benzoic acid	Observed heat of combustion	Reduction to standard initial conditions	Heat of combustion for standard initial conditions	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	g	*atm*	*int. joules*	*int. joules*	*int. joules*	*int. joules*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*
1	1.5263$_6$	29.9	40394.$_0$	10.$_3$	23.$_0$	40360.$_7$	26442.$_4$	−0.8	26441.$_6$	+3.5		
2	1.4943$_5$	30.3	39540.$_7$	11.$_6$	23.$_0$	39506.$_1$	26436.$_9$	−0.9	26436.$_0$	−2.1		
3	1.5422$_3$	22.2	40791.$_4$	11.$_6$	23.$_0$	40756.$_8$	26427.$_1$	+3.2	26430.$_3$	−7.8		
4	1.5172$_3$	22.0	40170.$_9$	11.$_6$	23.$_0$	40136.$_3$	26453.$_7$	+3.5	(26457.$_2$)			
5	1.5070$_5$	21.9	39883.$_9$	11.$_6$	23.$_0$	39849.$_3$	26441.$_9$	+3.5	26445.$_4$	+7.3		
6	1.4870$_3$	21.8	39339.$_3$	12.$_3$	23.$_0$	39304.$_0$	26431.$_2$	+3.6	26434.$_8$	−3.3	26438.$_1$	+3.2
7	1.4764$_3$	22.1	39067.$_8$	13.$_6$	23.$_0$	39031.$_2$	26436.$_2$	+3.4	26439.$_6$	+1.5		
8	1.5034$_4$	22.1	39769.$_6$	12.$_9$	23.$_0$	39733.$_7$	26428.$_5$	+3.4	26431.$_9$	−6.2		
9	1.5044$_9$	22.0	39817.$_5$	11.$_0$	23.$_0$	39783.$_5$	26443.$_2$	+3.5	26446.$_7$	+8.6		
10	1.4995$_0$	21.8	39672.$_6$	12.$_3$	23.$_0$	39637.$_3$	26433.$_6$	+3.6	26437.$_2$	−0.9		
11	1.4939$_6$	21.8	39526.$_7$	12.$_3$	23.$_0$	39491.$_4$	26434.$_0$	+3.6	26437.$_6$	−0.5		

MATERIAL NOT DRIED

12	1.4840$_2$	21.4	39256.$_4$	9.$_0$	23.$_0$	39224.$_4$	26431.$_1$	+3.8	26434.$_9$	+1.0		
13	1.4723$_4$	21.0	38952.$_8$	10.$_3$	23.$_0$	38919.$_5$	26433.$_7$	+4.0	26437.$_7$	+3.8		
14	1.5589$_7$	20.8	41244.$_4$	16.$_1$	23.$_0$	41205.$_3$	26431.$_1$	+4.0	26435.$_1$	+1.2	26433.$_9$	−1.0
15	1.4766$_1$	20.6	39061.$_6$	23.$_2$	23.$_0$	39015.$_4$	26422.$_2$	+4.2	26426.$_4$	−7.5		
16	1.5310$_1$	20.2	40509.$_1$	16.$_8$	23.$_0$	40469.$_3$	26433.$_0$	+4.4	26437.$_4$	+3.5		
17	1.5104$_7$	20.0	39952.$_3$	11.$_6$	23.$_0$	39917.$_7$	26427.$_3$	+4.5	26431.$_8$	−2.1		

MATERIAL FUSED

18	1.4920$_7$	20.1	39465.$_6$	15.$_5$	23.$_0$	39427.$_1$	26424.$_4$	+4.5	26428.$_9$	−5.4		
19	1.5286$_2$	20.2	40434.$_4$	9.$_7$	23.$_0$	40401.$_7$	26430.$_2$	+4.4	26434.$_6$	+0.3		
20	1.5167$_2$	20.1	40126.$_1$	11.$_6$	23.$_0$	40091.$_5$	26433.$_0$	+4.5	26437.$_5$	+3.2	26434.$_3$	−0.6
21	1.5174$_0$	20.2	40145.$_8$	12.$_9$	23.$_0$	40109.$_9$	26433.$_3$	+4.4	26437.$_7$	+3.5		
22	1.5243$_4$	20.●	40320.$_5$	11.$_6$	23.$_0$	40285.$_9$	26428.$_4$	+4.5	26432.$_9$	−1.4		

MATERIAL DRIED AT 105° C												
36	1.5159$_6$	29.4	40108.$_3$	10.$_0$	23.$_0$	40075.$_3$	26435.$_6$	−0.5	26435.$_1$	+1.6	26433.$_5$	−1.4
37	1.5151$_1$	29.4	40090.$_9$	9.$_7$	23.$_0$	40058.$_2$	26439.$_1$	−0.5	26438.$_6$	+5.1		
38	1.5236$_2$	29.5	40293.$_9$	9.$_0$	23.$_0$	40261.$_9$	26425.$_1$	−0.5	26424.$_6$	−8.9		
39	1.5222$_9$	29.7	40276.$_1$	9.$_0$	23.$_0$	40244.$_1$	26436.$_5$	−0.7	26435.$_8$	+2.3		
40	1.5120$_1$	29.6	40001.$_8$	10.$_0$	23.$_0$	39968.$_8$	26434.$_2$	−0.6	26433.$_6$	+0.1		
MATERIAL FUSED												
23	0.9892$_7$	20.4	26170.$_8$	9.$_0$	23.$_0$	26138.$_8$	26422.$_2$	+5.7	26427.$_9$	−2.1	26430.$_0$	−4.9
24	.9991$_3$	20.2	26431.$_7$	7.$_7$	23.$_0$	26401.$_0$	26424.$_0$	+5.9	26429.$_9$	−0.1		
25	.9988$_0$	20.1	26418.$_6$	9.$_0$	23.$_0$	26386.$_8$	26418.$_5$	+5.8	26424.$_3$	−5.7		
26	1.0166$_3$	20.4	26765.$_8$	10.$_3$	23.$_0$	26732.$_5$	26425.$_2$	+5.6	26430.$_8$	+0.8		
27	.9973$_5$	20.2	26392.$_7$	8.$_4$	23.$_0$	26361.$_3$	26431.$_1$	+5.8	26436.$_9$	+6.9		
MATERIAL NOT DRIED												
41	0.9997$_7$	21.5	26436.$_3$	7.$_1$	23.$_0$	26405.$_2$	26412.$_3$	+5.1	26417.$_4$	−12.7	26430.$_1$	−4.8
42	1.0035$_0$	22.5	26564.$_2$	8.$_7$	23.$_0$	26532.$_5$	26440.$_0$	+4.7	26444.$_7$	+14.6		
43	.9954$_4$	21.6	26333.$_7$	6.$_0$	23.$_0$	26304.$_7$	26425.$_2$	+5.1	26430.$_3$	+0.2		
44	1.0146$_9$	21.6	26837.$_6$	7.$_3$	23.$_0$	26807.$_3$	26421.$_5$	+5.0	26426.$_5$	−3.6		
45	1.0075$_4$	21.4	26655.$_1$	7.$_3$	23.$_0$	26624.$_8$	26425.$_5$	+5.1	26430.$_6$	+0.5		
46	.9960$_3$	21.3	26353.$_4$	9.$_1$	23.$_0$	26321.$_3$	26426.$_2$	+5.2	26431.$_4$	+1.3		
MATERIAL DRIED AT 105° C												
28	0.7026$_6$	20.5	18592.$_0$	5.$_2$	23.$_0$	18563.$_8$	26419.$_3$	+6.4	26425.$_7$	−4.6	26430.$_3$	−4.6
29	.6800$_1$	20.1	17995.$_7$	5.$_8$	23.$_0$	17966.$_9$	26421.$_4$	+6.7	26428.$_1$	−2.1		
30	.6987$_0$	20.1	18496.$_9$	7.$_1$	23.$_0$	18466.$_8$	26430.$_3$	+6.7	26437.$_0$	+6.7		
31	.6992$_0$	20.0	18484.$_7$	3.$_2$	23.$_0$	18458.$_8$	26399.$_8$	+6.7	(26406.$_2$)			
MATERIAL DRIED AT 105° C												
32	1.9955$_1$	29.8	52788.$_7$	11.$_6$	23.$_0$	52754.$_1$	26436.$_4$	−2.0	26434.$_4$	−0.7	26435.$_1$	+0.2
33	2.0188$_9$	29.6	53419.$_8$	12.$_3$	23.$_0$	53384.$_8$	26442.$_4$	−1.9	26440.$_5$	+5.4		
34	2.0242$_9$	29.6	53542.$_0$	11.$_6$	23.$_0$	53507.$_4$	26433.$_8$	−1.9	26431.$_9$	−3.2		
35	2.0294$_1$	29.5	53685.$_4$	14.$_2$	23.$_0$	53648.$_2$	26435.$_3$	−1.8	26433.$_5$	−1.6		
Mean of all observations except experiments 4 and 31									26433.$_8$			
Mean of 39d and 39e									26434.$_9$			

Reduction to the standard state practically always brought the results of groups of experiments made under different conditions into better agreement. It is seen from tables 7 and 8, however, that even after reduction to the standard state there are small systematic differences between the results of measurements made at different times and under different conditions. Thus the results obtained with 1.5 g samples of benzoic acid are, in general, somewhat higher than those obtained with 1.0 g samples. This difference is consistent with the apparent variation of the electrical energy equivalent of the calorimeter with temperature rise discussed in section III of this paper. However, since this variation was not observed in all cases, either in the calibration of the calorimeter or in the combustion experiments, it seems best to take the mean of the results of all experiments as the best value deducible from the present work for the heat of combustion of the standard samples.

In taking the mean of the results on sample 39d, experiments 1 to 6, inclusive, were disregarded, as the oxygen used in these experiments was not purified, and may have contained combustible impurities. The mean of the results of these experiments is definitely higher than the mean of the results of any other group of experiments, and 0.03 percent higher than the mean result obtained for this sample. Experiments 58 to 63 were also disregarded (although including them would not have changed the mean of all of the experiments) because in these experiments a large piece of the glass used to insulate the firing electrode was placed in the bottom of the bomb. The results of these experiments indicate that the action on the glass of the nitric acid formed in the combustion does not produce any appreciable thermal effect. Experiments 7, 40, and 56 were disregarded on account of very large differences from the other experiments.

In taking the mean of the results on sample 39e experiments 4 and 31 were disregarded, the former on account of a short circuit in the firing circuit which resulted in a large firing energy, and the latter on account of a large change in the temperature of the jacket during the experiment.

The mean results for samples 39d and 39e are, respectively, 26,436 and 26,434 international joules per gram weight in air against brass weights. As the 2 values differ by less than the estimated uncertainty of the results, the average of the 2 values, 26,435 international joules per gram weight of air, or 26,414 international joules per gram mass (weight corrected for air buoyancy)[20] may be taken as the heat of combustion of either sample under the standard conditions mentioned above.

The average deviation of the individual results of electrical energy experiments from the mean is 2.1 int. joules per degree, or 0.015 percent. The average deviation of the individual results of heat of combustion determinations from the mean is 5.0 int. joules per gram, or 0.019 percent. On account of the large number of observations the probable errors of the final results of both the electrical energy experiments and the heat of combustion measurements are absurdly small (less than 0.002 percent). The probable error of a single electrical energy experiment is 1.8_5 international joules per degree (0.014

[20] The correction for air buoyancy is based on the assumption that the densities of benzoic acid, weights, and air are, respectively, 1.26, 8.4, and 0.00117 g/cm³. The value used for the density of air is the average value calculated from 16 observations of temperature and barometric pressure made during the course of the work. The individual values of density of air varied from 0.00115 to 0.00120 g/cm³.

percent). The probable error of a single heat of combustion measurement is 4.3 international joules per gram (0.016 percent). The estimated uncertainty in the final result is 6 international joules per gram (0.023 percent). The value for the heat of combustion obtained by combining the highest mean observed electrical energy equivalent of the calorimeter for a group of experiments (experiments 5 to 9 and 16 to 20 in table 3), with the highest mean observed heat of combustion for a group of experiments (experiments 8 to 23 and 50 to 52 in table 7, or experiments 1 to 11 in table 8), would be higher than that given above by 0.04 percent. Similarly, the value obtained by combining the lowest mean observed electrical energy equivalent for a group of experiments with the lowest mean heat of combustion for a group of experiments, would be lower than the value given above by 0.05 percent.

The measurements were made at 30° C as a matter of convenience, since often during the summer months it is not possible to keep the jacket at a lower temperature. Most thermochemical data are, however, referred to 25° C. Using specific heat data given in International Critical Tables, vol. 5, 80 and 104, the temperature coefficient of the heat of combustion of benzoic acid is found to be −0.94 joule per gram per °C. The heat of combustion at 25° C is then 26,440 international joules per gram weight of air against brass weights, or 26,419 international joules per gram mass, when the sample is burned at 25° C in oxygen under an initial pressure of 30 atmospheres,[21] the mass of sample and the mass of water placed in the bomb initially each being 3 g per liter of bomb volume.[22] This value is for the heat of combustion of the standard samples 39d and 39e, neither of which is absolutely pure benzoic acid, although the amount of impurity is known to be small.

V. PREVIOUS WORK

Fischer and Wrede [23] in 1909 reported the results of 7 determinations of the heat of combustion of benzoic acid. The mean of the 7 observations was 26,475 joules per gram mass at about 17.5 °C, with an average deviation from the mean of 6 joules per gram.

The oxygen pressure used in these measurements was 45 atmospheres, the volume of the bomb 275 cm^3, the mass of charge about 0.9 g, and the mass of water placed in the bomb before each experiment 0.5 g.

The calorimeter was calibrated electrically by Jaeger and von Steinwehr,[24] who made 13 determinations, the average deviation from the

[21] Strictly speaking the value given for the heat of combustion at 25° corresponds to an initial oxygen pressure of 29.5 atmospheres, since it is derived from the value at 30° and 30 atmospheres by the use of data on C_V, and since on cooling from 30 to 25° C the initial pressure would decrease by 0.5 atmosphere. The difference is of no importance as a difference of 0.5 atmosphere in the initial pressure results in a change of only 0.001 percent in the observed heat of combustion.

[22] The heat of combustion under conditions differing from the standard conditions is obtained by multiplying the value given by the factor

$$1+10^{-4}[25(P-30)+49\left(\frac{M_s}{V}-3\right)+38\left(\frac{M_w}{V}-3\right)-36(t-25)]$$

where

P=initial absolute pressure of oxygen in atmospheres.
M_s=mass of sample of benzoic acid, in grams.
M_w=mass of water in bomb before combustion, in grams.
V=volume of bomb in liters.
t=temperature to which reaction is referred, in °C.

[23] Z.phys.Chem. **69**,218(1909).

[24] Ann.d.Phys. **21**,23(1906).

mean being 0.04 percent. The unit of electromotive force used in this calibration was based on the value 1.01860 volts for the emf of the Weston cell, whereas the accepted value of the emf of the Weston cell in terms of the present international volt is 1.01830.

Hence the value obtained by Fischer and Wrede, when expressed in terms of the present international electrical units, will be less than the value given above by 0.06 percent, or 16 joules per gram. According to Jaeger and von Steinwehr [25] a further correction of −8 joules per gram should be applied to take account of the firing energy. The value is still further lowered by 7 joules per gram by reduction to the standard temperature of 25° C, and by 7 joules per gram by reduction to the standard initial conditions. The finally recomputed value is therefore 26,437 international joules per gram mass.

Wrede [26] in 1910 made 7 additional measurements of the heat of combustion of benzoic acid in the same calorimeter and under the same conditions as in the measurements of Fischer and Wrede. The mean of the results obtained was 26,466 joules per gram mass. Application of the corrections mentioned above yields the value 26,428 international joules per gram mass at 25° C and under the standard initial conditions.

Dickinson [27] in 1914 reported the value 6,329 calories_{20} per gram weight in air against brass weights, as the mean of a large number of measurements of the heat of combustion of benzoic acid. The measurements were made at about 25° C, the initial oxygen pressure was 30 atmospheres, the volume of the bomb 275 cm^3, the mass of charge 1.5 g, and the mass of water placed in the bomb before each experiment was 0.5 g. The calorimeter was calibrated in terms of the present international electrical units, and the method of reduction to calories is equivalent to the use of a conversion factor of 4.181 joules per calorie_{20}.

Upon converting to electric units by means of the factor given above, and correcting for air buoyancy, Dickinson's value becomes 26,441 international joules per gram mass. Reduction to the standard initial conditions lowers this value to 26,439 international joules per gram mass.

It has recently been pointed out by D. R. Harper, 3d [28] that, in calculating the heat capacity of the oxygen in his bomb, Dickinson used C_p rather than C_v. The difference amounts to 0.02 percent in the total heat capacity of the calorimeter, and the resulting value for the heat of combustion of benzoic acid is therefore too high by this amount. On reducing the value given above by 0.02 percent, the finally recomputed value becomes 26,434 international joules per gram mass.

Roth, Doepke, and Banse [29] in 1928 reported the results of 2 series of measurements with an electrically calibrated calorimeter, of the heat of combustion of benzoic acid. The material used was supplied by Kahlbaum, and tested by P. Verkade, in Rotterdam, according to whom it was identical, so far as heat of combustion measurements indicated, with material obtained from the National Bureau of Standards. (Probably standard sample 39d.)

[25] Z. Phys. Chem. **135**, 305 (1928).
[26] Z. phys. Chem. **75**, 81 (1910).
[27] Bul. BS **11**, 189 (1914); S230.
[28] Private communication.
[29] Z. phys. Chem. **133**, 431 (1928).

The first series consisted of 7 calibration experiments in which the average deviation from the mean was 0.04 percent, and 7 combustion experiments with an average deviation from the mean of 0.035 percent. The second series consisted of 6 calibration experiments and 5 combustion experiments, the average deviations from the means being 0.05 and 0.025 percent, respectively. The difference in the values of the heat of combustion obtained in the 2 series was 0.02 percent.

Temperatures were measured by means of a Beckmann thermometer. The initial oxygen pressure was 35 atmospheres; the mass of the sample varied from 0.5 to 0.9 g. The volume of the bomb and the mass of water placed in it are not given. Washburn[30] in reducing the result to the standard initial state, has assumed that the bomb volume was 0.3 liter, and the mass of water placed in the bomb was 1.0 g.

The value reported by Roth, Doepke, and Banse is 26,433 international joules per gram mass, at 20° C. Reduction to the standard initial state and to 25° C lowers this value to 26,426 international joules per gram mass.

According to measurements made in 1931 and reported by Vinal,[31] there is a difference in the value of the watt derived from electrical standards maintained at the Physikalischtechnische Reichsanstalt, and that derived from standards maintained at the National Bureau of Standards, the latter being larger by 0.013 percent. Hence the result obtained by Roth, Doepke, and Banse, when expressed, for the purpose of comparision with the results of the present work, in terms of the electric units maintained at this Bureau, becomes 26,423 international joules per gram mass at 25° C.

Jaeger and von Steinwehr[32] in 1928 reported the results of measurements of the heat of combustion of benzoic acid, using the calorimeter and bomb which had been used by Fischer and Wrede. Two lots of material were used, one obtained from the National Bureau of Standards and the other supplied by Kahlbaum and tested by Verkade. The oxygen pressure used was 45 atmospheres, the volume of the bomb 280 cm^3, and the mass of the charge of benzoic acid 0.9 g. The mass of water placed in the bomb is not given, but may be assumed to be 0.5 g as in the measurements of Fischer and Wrede.

The calorimeter was calibrated electrically, and a platinum resistance thermometer used for temperature measurements. Two series of determinations of the heat capacity were made, which gave results differing by 0.067 percent. The average deviation from the mean in the first series was 0.07 percent and in the second 0.08 percent.

Seven combustion measurements on the National Bureau of Standards material gave the value 26,444 international joules per gram mass at 20° C, while 9 determinations with the Kahlbaum material gave the value 26,433 international joules per gram mass. The average deviation from the mean for each material was ± 17 joules per gram. On reducing to 25° C and the standard initial state, and correcting for the difference in the watt, these 2 values become 26,426 and 26,415 respectively, in terms of the international electrical units maintained at the National Bureau of Standards. The mean of all of the experiments on both materials is 26,420 international joules

[30] BS J. Research **10**, 525 (1933); RP546.
[31] BS J. Research, **8**, 729 (1932); RP448.
[32] Z. phys. Chem. **135**, 305(1928).

per gram mass, which is practically identical with the value obtained in the present work for the National Bureau of Standards material.

The results obtained by the various observers are summarized in table 9. The value obtained in the present work is seen to be in

TABLE 9.—*Results obtained by various observers*

Observer	Date	Heat of combustion at 25° C and standard initial state
		int. joules/g (vac)
Fischer and Wrede	1909	26,437
Wrede	1910	26,428
Dickinson	1914	26,434
Roth, Doepke, and Banse	1928	26,423
Jaeger and von Steinwehr	1928	[1] 26,426 [2] 26,415
Present work	1933	26,419

[1] National Bureau of Standards Material.
[2] Kahlbaum-Verkade Material.

agreement within 0.03 percent[33] with the values obtained by Roth, Doepke, and Banse, and by Jaeger and von Steinwehr. The value obtained by Wrede in 1910 is higher by 0.03_4 percent, while those of Fischer and Wrede and of Dickinson are, respectively, 0.07 and 0.06 percent higher than the value obtained in the present work.

It is not possible to say how much of these differences is due to differences in material and how much to experimental errors. The results obtained in the present work indicate that a part of the differences may be due to combustible impurities in the oxygen used. Fischer and Wrede analyzed their oxygen for hydrogen and hydrocarbons, and state that no detectable amount of either was present. They give no data on the accuracy of their analyses, but their method can be used with sufficient accuracy to detect an amount of impurity which would cause an error of 0.01 percent in the heat of combustion. Dickinson used atmospheric oxygen which was obtained commercially and did not determine or remove combustible impurities. If this oxgyen contained the same amount of combustible impurities as that used in the present work, and if the error caused by these impurities is proportional to the mass of oxygen in the bomb, a correction of −0.02 percent should be added to Dickinson's value which would bring it within 0.04 percent of the value obtained in the present work. Roth, Doepke, and Banse give no data regarding the oxygen used in their work. Jaeger and von Steinwehr state that they used commercial oxygen which was obtained from liquid air, and was "very pure."

VII. SUMMARY

Measurements of the electrical energy equivalent of a bomb calorimeter, and of the heat of combustion of two lots of benzoic acid are described. The value obtained for the heat of combustion of these lots at 25° C is 26,419 international joules per gram mass (weight corrected for air buoyancy) when the sample is burned in an enclosure of constant volume, in oxygen under an initial pressure of 30 atmos-

[33] Within 0.015 percent if the results of Jaeger and von Steinwehr are all averaged together.

pheres absolute, the mass of sample and mass of water placed in the bomb each being 3 g per liter of bomb volume. This is in agreement within 0.03 percent with measurements reported in 1928 by Roth, Doepke, and Banse, and by Jaeger and von Steinwehr, but is 0.07 percent lower than the value obtained by Fischer and Wrede, and 0.04 or 0.06 percent lower than that obtained by Dickinson. The differences may be due partly to differences in material, and partly to combustible impurities in the oxygen used by the previous investigators.

The work described in this paper was done under the direction of H. C. Dickinson and E. F. Mueller, both of whom have contributed valuable suggestions during the course of the work.

The chemical data on sample 39d were obtained by A. Isaacs, and those on sample 39e by J. I. Hoffman and H. A. Buchheit. The freezing point measurements on sample 39d were made by F. W. Rose. Several analyses of gaseous products of combustion for carbon monoxide were made by C. Creitz.

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AUTOGRAPHIC THERMAL EXPANSION APPARATUS

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ABSTRACT

This paper describes an autographic thermal expansion apparatus improved and constructed by the National Bureau of Standards, and indicates the methods used in its calibration and comparison with the Bureau's precision expansion apparatus. The autographic expansion apparatus employs the optical lever method of measuring expansion and is suitable for many purposes in commercial laboratories. Continuous expansion curves can be obtained photographically or they can be observed during the progress of the test. Coefficients of expansion can be determined from these curves. Transformation regions, if present, can also be located. For ordinary materials such as steel, it may be stated that the error of the autographic expansion apparatus is about 6 percent for the range from 20 to 100° C and about 3 percent for the range from 20 to 500° C. This apparatus does not give as accurate results as the fused quartz tube expansion apparatus which was also designed at the Bureau for use in commercial laboratories. The autographic expansion apparatus yields certain information in regard to transformation regions not readily obtainable by the other type of apparatus.

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I. INTRODUCTION

In 1924 the National Bureau of Standards made tests on an autographic thermal expansion apparatus which was built abroad and submitted to the Bureau by a local firm for test. Thermal expansion tests were made on eight samples of various materials. A comparison of the coefficients of expansion determined with this apparatus and with the precision expansion apparatus [1] of the Bureau, showed that the average error of this autographic expansion apparatus was ±12 percent.

Several years later the Bureau decided to design and construct an apparatus of similar type [2] but which would give more accurate results and would be suitable for use in commercial laboratories.

The autographic expansion apparatus developed employs the optical lever method of measuring thermal expansion. With this apparatus it is possible to obtain expansion curves photographically

[1] Souder and Hidnert, BS Sci. Pap. 22,533(1927-28);S524.

[2] Autographic expansion apparatus has been employed by Chevenard (Revue de Métallurgie, 19,39(1922) and 23,92(1926), and others.

or to observe points on the expansion curves of materials during the progress of the test. The latter method is preferable in many cases, for the observer can see and follow every detail in the generation of the expansion curve during the progress of the test and can modify or stop the test whenever necessary, but with the photographic method nothing is known about the expansion curve until the test has been completed and the sensitized plate or paper has been developed.

The autographic expansion apparatus will supply data on the thermal expansion of materials, with sufficient accuracy to meet the needs of many commercial laboratories. This apparatus, however, is not as accurate as the fused quartz tube type [3] of thermal expansion apparatus, which was also designed for use in commercial laboratories. The autographic apparatus will be found especially useful in locating transformation regions. Where necessary to make complete and accurate studies of a specimen in such regions, this apparatus will be of value in locating the approximate temperature limits within which to confine measurements with precision apparatus.

The authors are indebted to E. C. Crittenden, H. W. Bearce, and C. G. Peters for valuable suggestions, to F. E. Mann for his painstaking work in the construction of the apparatus, to H. S. Krider for assistance during the calibration and the tests of the apparatus, and to S. Alpher for assistance in the preparation of the figures.

II. DESCRIPTION OF APPARATUS

Two general views of the autographic expansion apparatus are shown in the photographs, figures 1 and 2. The apparatus consists essentially of an adjustable furnace, F, mounted on a common base with a camera box, C, and an adjustable source of illumination, I. The overall length is approximately 64 in.,[4] height 19 in., and width 14 in. A description of the furnace, the optical system, and auxiliary parts is given in this section. It is planned to prepare detailed drawings later so that copies may be available to persons interested in constructing such equipment.

The heating coil of the furnace consists of chromel A wire wound on an alundum cylinder 2 in. outside diameter and 8 in. in length. The wire, about 19½ ft long and 0.0907 in. diameter (American Wire Gage no. 11), has a total resistance of 1.65 ohms. Grooves were cut in the alundum cylinder to receive the heating coil. Near the ends the coil was wound as close as possible without short circuiting, and the spacing was increased toward the center. The spacing at the central turn is ½ in. There are 15 turns of wire for the first 2 in., 15 turns for the last 2 in. and 11 turns for the central 4 in. of the coil. Asbestos cord was wrapped between the wire, and was sealed up with alundum cement. The alundum cylinder has 4 holes, each ⅝ in. in diameter, through the entire length of the cylinder. The wall space between the holes is 1/16 in. A copper tube, 8 in. long and 2¾ in. inside diameter, and machined as indicated in figure 3, surrounds the heating coil. A larger brass tube (nickel plated) about 12 in. long and 6 in. outside diameter, surrounds the copper tube. Silocel insulating powder was inserted between the copper and the brass

[3] Hidnert and Sweeney, BS J.Research, 1,771 (1928); RP29.

[4] English and metric units may appear to be used indiscriminately throughout this paper. An attempt has been made, however, to give dimensions and sizes in the units which are commonly given in catalog and shop records.

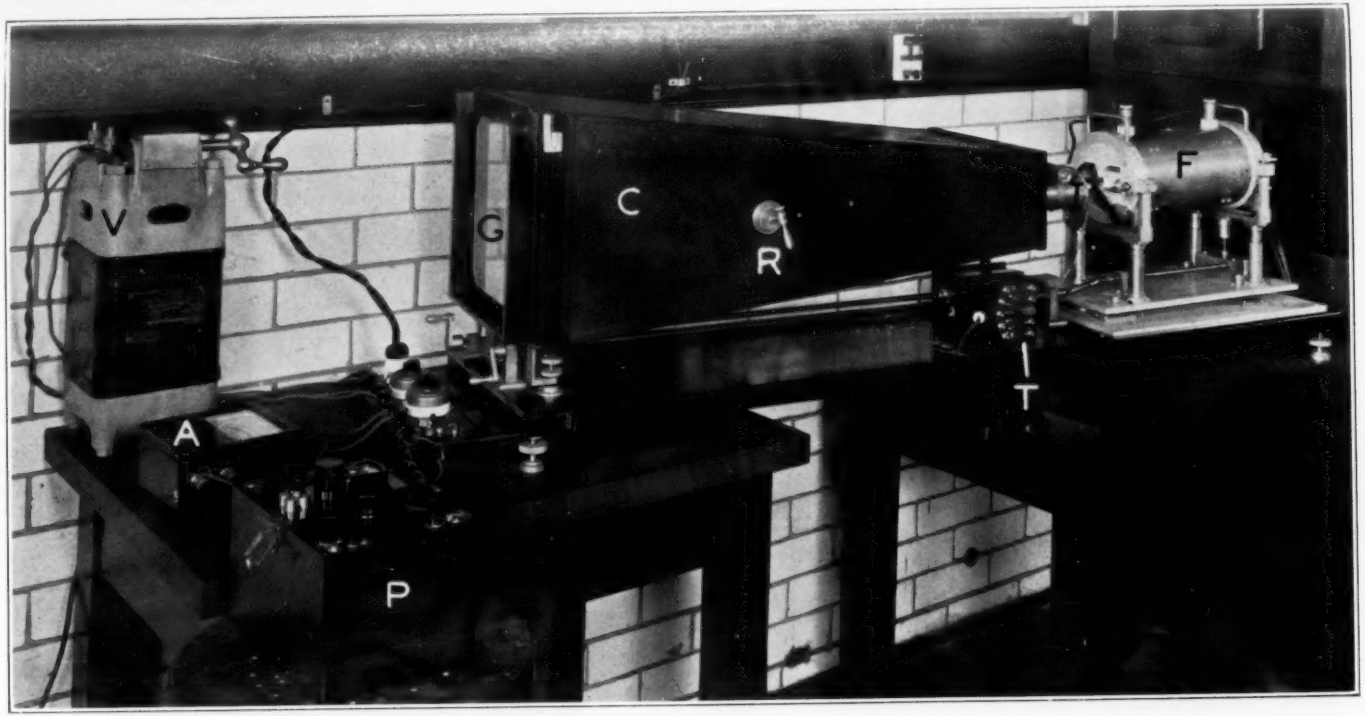

FIGURE 1.—*Autographic expansion apparatus.*

A, Ammeter; *C*, camera box; *F*, furnace; *G*, glass screen; *I*, illumination; *P*, potentiometer indicator *R*, internal reflecting mirror; *T*, transformer; *V*, induction voltage regulator.

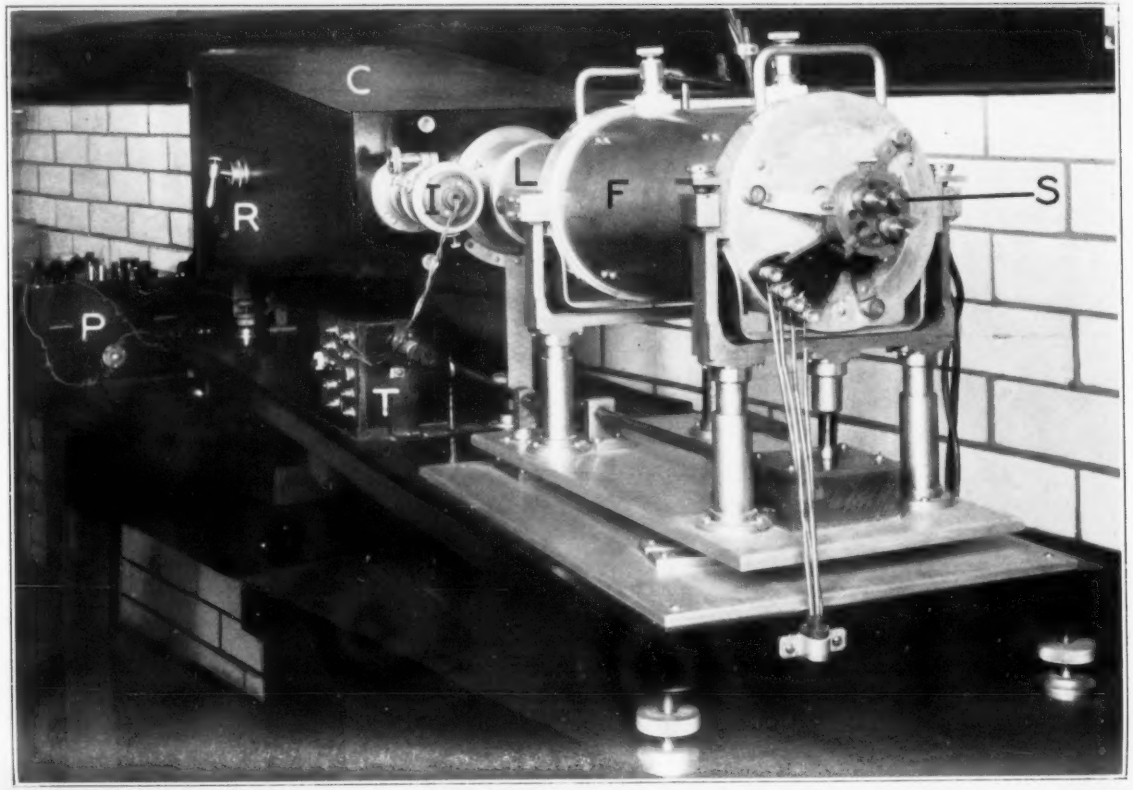

FIGURE 2.—*Autographic expansion apparatus.*

C, Camera box; *F*, furnace; *I*, illumination; *L*, lens; *P*, potentiometer indicator; *R*, internal reflecting mirror; *S*, adjusting screw ; *T*, transformer.

tubes. The insulation was continued around the ends of the 8 in. copper tube. The furnace is supported in a horizontal position, with the lead-in wires at the top of the furnace.

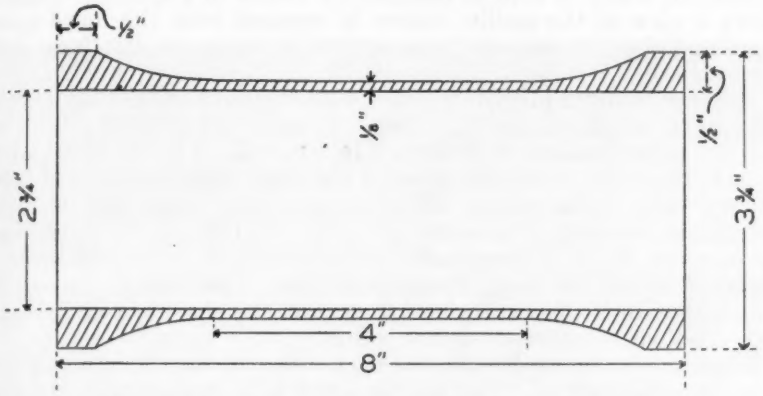

FIGURE 3.—*Copper tube surrounding the heating coil.*

Through each hole in the alundum cylinder (see fig. 4) a chromel tube was inserted. The following materials were inserted in the chromel tubes as indicated:

Hole 1.—A long, fused-quartz rod which represents a "stationary" axis. Details of the fused-quartz rod are indicated in figure 5. The finish on point (a) is smooth and suitable for making contact in a bearing similar to that shown at (b). The finish on bearing (b) is smooth and suitable for receiving a point similar to (a). The drilled relief (c) is a small hole having a smooth edge giving a circular contact closely approximating a point contact.

Hole 2.—A rod of chromel A having uniform rate of expansion, 150 mm in length, which represents a temperature axis.

Hole 3.—A specimen 150 mm in length, with pointed ends. The maximum diameter of the specimen is 12 mm.

Hole 4.—A chromel-alumel thermocouple with 3 junctions, 1 near the center of the specimen in hole 3 and the other junctions near the ends of the specimen.

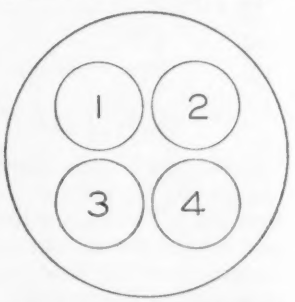

FIGURE 4.—*Cross section of alundum cylinder indicating the holes and the positions of specimen, "stationary" axis, temperature axis, and thermocouple.*

1, "Stationary" axis; 2, temperature axis; 3, specimen (expansion axis); 4, thermocouple. The observer is located at the glass screen, G, of the camera box (fig. 1) and is looking toward the furnace.

The ends of the rod of chromel and the specimen in holes 2 and 3, respectively, are pointed. The angle at each pointed end is about 80°.

A fused-quartz plug is in contact with each end of the chromel rod (temperature axis) and of the specimen. The plugs in contact with the left [5] ends (see fig. 6) of the chromel rod and the specimen have the same dimensions as the long, fused-quartz rod indicated in figure 5,

[5] Unless indicated otherwise, the direction "left" or "right" orients the observer so that he is facing the furnace, F, with the camera box, C, at his left.

except that the length is 4⅞ in. The pointed ends of these 2 plugs and of the long, fused-quartz rod ("stationary" axis) extend beyond the left face of the furnace and are in contact with the rear of a stellite mirror, M, which is held in position by means of a spring. Figure 6 shows a view of the stellite mirror in contact with the fused-quartz plugs and the "stationary" axis extending from the left face of the furnace.

The fused-quartz plugs in contact with the right ends of the chromel rod and the specimen are 4 in. long. At each end of these plugs there is a 90° pivot bearing as indicated in figure 5. The diameter of the plugs is the same as the diameter of the long, fused-quartz rod ("stationary" axis). One end of each of these plugs and one end (90° pivot bearing) of the long, fused-quartz rod extend beyond the right face of the furnace. Each of these ends is held against an adjustable screw, S. Figure 7 shows the long, fused-quartz rod ("stationary" axis), the specimen with its 2 fused-quartz plugs and the chromel rod (temperature axis) with its 2 fused-quartz plugs.

When the furnace is heated, the specimen and the chromel rod (temperature axis) expand. The mirror which is in contact with the plugs extending from the specimen, chromel rod (temperature axis) and

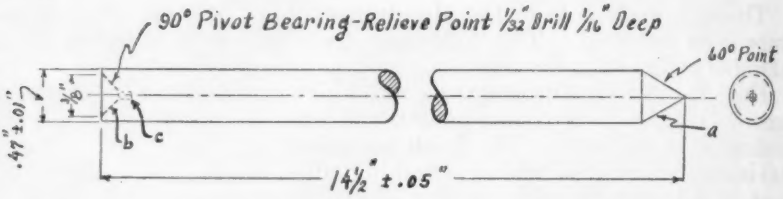

FIGURE 5.—*Details of fused-quartz rod representing "stationary" axis.*

"stationary" axis therefore moves. The expansion of the specimen causes the bottom of the mirror to move and deflect the spot of light upward. The expansion of the chromel rod (temperature axis) causes one side of the mirror to move and deflect the spot horizontally. The expansion of the fused-quartz plugs extending on each side of the specimen should balance the expansion of the fused-quartz plugs extending on each side of the chromel rod (temperature axis) and also the expansion of an equivalent length of the "stationary" axis. A spot of light focused on the mirror and reflected on a glass screen, G, or photographic plate indicates the expansion both of the specimen and of the chromel rod and describes a curve, the resultant of these two expansions. The abscissas (from right to left)[6] indicate the expansion of the chromel rod (temperature axis) and may be evaluated to represent temperature. The ordinates (from bottom to top) represent the expansion of the specimen. The curve (see fig. 9) therefore represents the expansion of the specimen versus temperature in arbitrary units. This curve may be transformed into an expansion curve in definite units after the apparatus is calibrated.

In order to attain satisfactory temperature uniformity throughout the specimen chamber and the thermocouple chamber in the alundum cylinder, a large number of experiments were carried out on three heating coils with and without a tube surrounding the heating coil. Tubes

[6] The observer is located at the glass screen, G, of the camera box and is looking toward the furnace.

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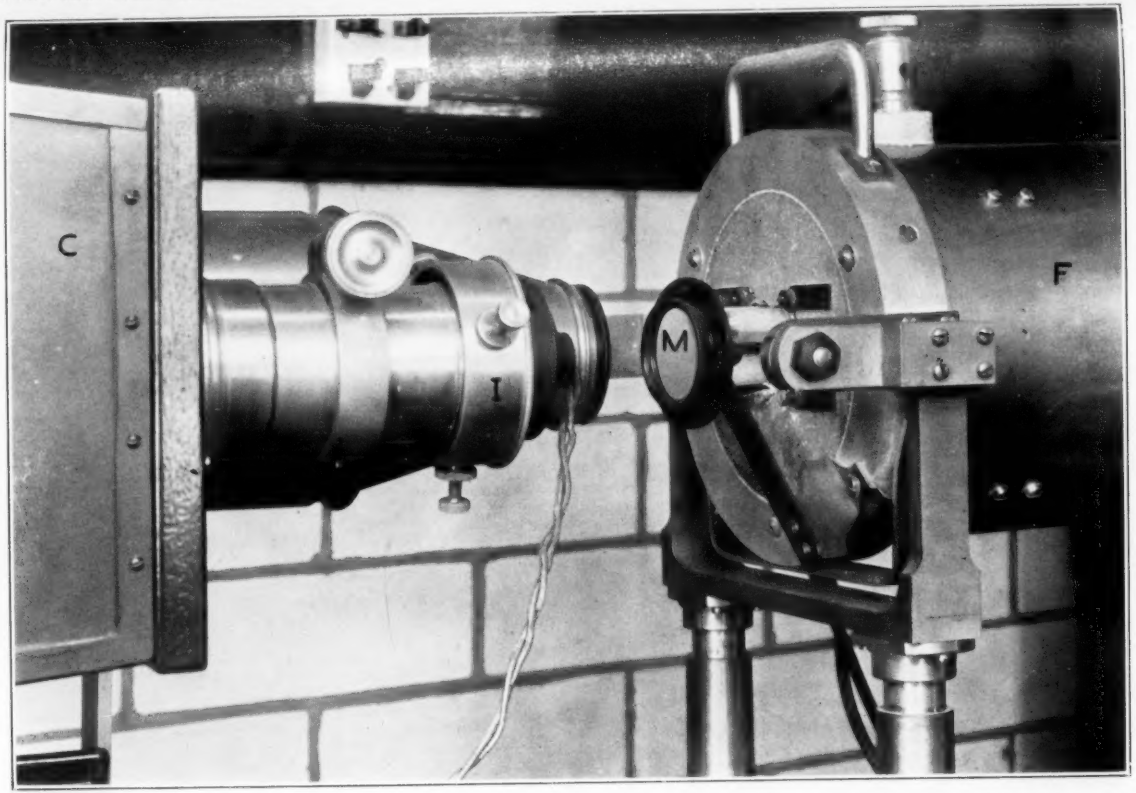

FIGURE 6.—*Stellite mirror in contact with the fused quartz plugs and the "stationary" axis extending from the left face of the furnace.*

C, Camera box; *F*, furnace; *I*, Illumination; *M*, optical lever mirror.

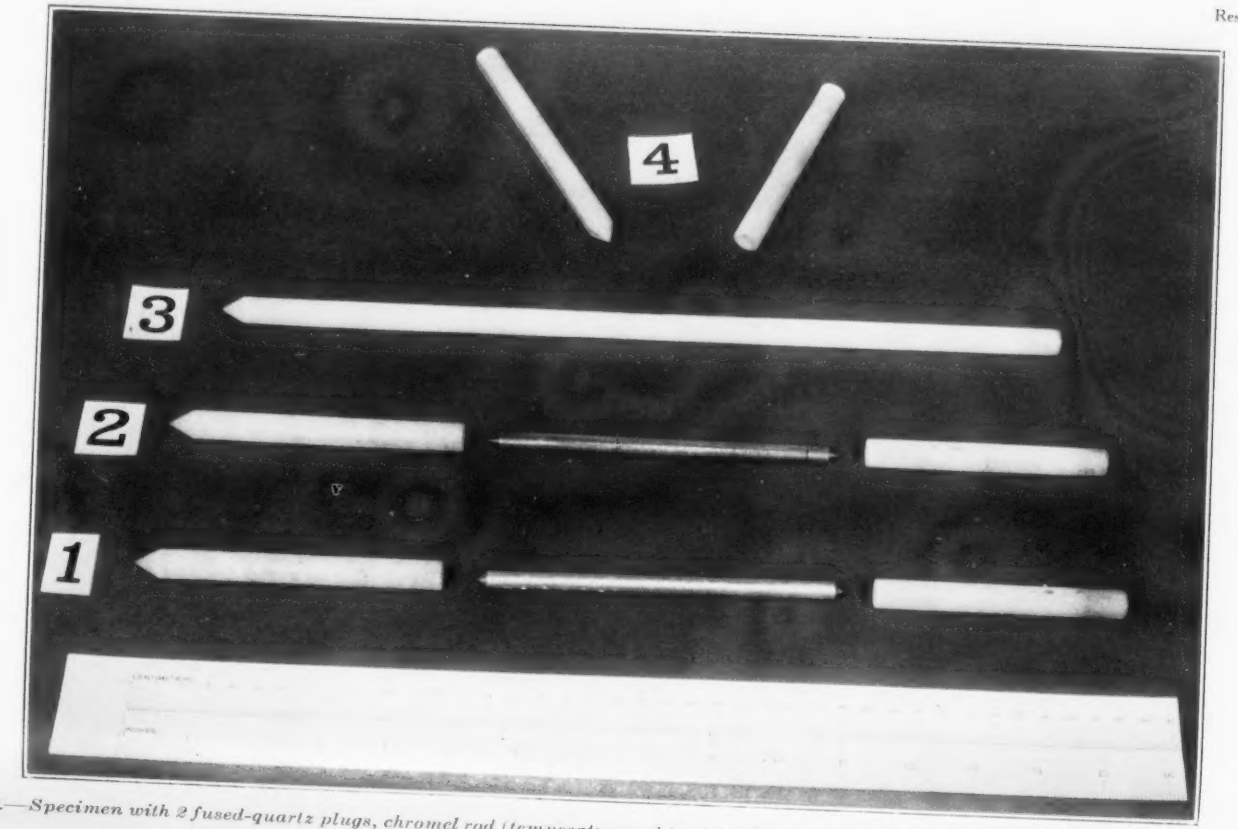

FIGURE 7.—*Specimen with 2 fused-quartz plugs, chromel rod (temperature axis) with 2 fused-quartz plugs and long fused quartz rod ("stationary" axis).*

1, Specimen and 2 plugs; *2*, chromel rod (temperature axis) and 2 plugs; *3*, long fused-quartz rod ("stationary" axis); *4*, two extra plugs showing ends.

of uniform thickness, made of iron, copper, and copper plated with nickel and a copper tube of nonuniform thickness (see fig. 3) were tried. Experiments were also made with plugs of various shapes and kinds (chromel, porcelain, and fused quartz). The best temperature uniformity was obtained with the heating coil, copper tube, and fused-quartz plugs which have been described. The temperature distribution at various points in the specimen chamber and the thermocouple chamber was explored at about 250°, 500°, and 800° C. An exploring thermocouple was used in the specimen chamber and the thermocouple (with three junctions) which was described previously was used in the thermocouple chamber. Figure 8 shows the results obtained. Position 3 represents the center of the specimen chamber and the thermocouple chamber. Position 0 represents a point 75 mm to the left of position 3, and position 6 represents a point 75 mm to the right of position 3 in these chambers. Positions 1, 2, 4, and 5 are intermediate positions. Between positions 0 and 6 the distance from one position

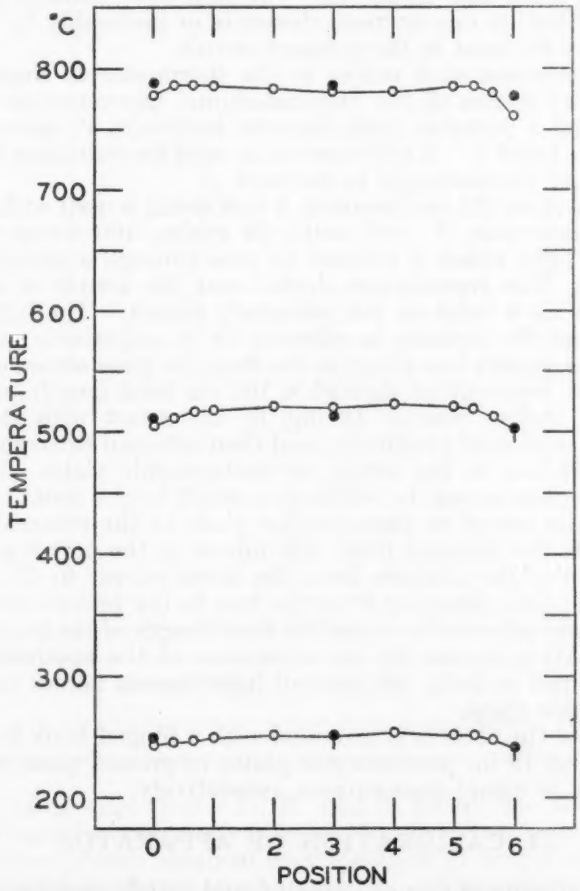

FIGURE 8.—*Distribution of temperature at various positions (position 3=center) in specimen chamber and thermocouple chamber.*

○ Specimen chamber; ● Thermocouple chamber; ⚲ Specimen and thermocouple chambers.

to the next position is 25 mm. Position 3 corresponds to the center of the specimen and positions 0 and 6 correspond to the ends of the specimen in the specimen chamber. The observations in figure 8 show that the temperatures in the specimen chamber agree well with those in the thermocouple chamber. At the extreme positions (0 and 6) the temperatures are somewhat lower than at the central position.

The furnace is heated by passing electric current through the coil described. An induction voltage regulator, V (primary 110 volts, 60 cycles), and an ammeter, A, were inserted in the circuit. These instruments are shown at the extreme left of figure 1. By means of the induction voltage regulator it is possible to obtain any current required to heat and maintain the furnace at any temperature between room temperature and 1,000° C. The induction voltage regulator may be replaced by one or more rheostats or preferably by a transformer with a rheostat in the primary circuit.

The temperatures at 3 points in the thermocouple chamber are determined by means of the chromel-alumel thermocouple (with 3 junctions) and a portable potentiometer indicator, P, shown at the left of figures 1 and 2. A triple switch is used for switching from one junction of the thermocouple to the next.

A tungsten lamp (21 candlepower, 6 to 8 volts) is used with a multivolt toy transformer, T (110 volts, 60 cycles, 100 watts type) to produce the light which is allowed to pass through a pinhole in the camera box. The transformer shown near the center of figures 1 and 2, is set for 6 volts on the secondary circuit. The light which passes through the pinhole, is reflected by an adjustable mirror, R, located in the camera box about 35 cm from the glass screen or photographic plate, transmitted through a 100 cm focal length lens, L, to the external stellite mirror, M (fig. 6) in contact with the fused-quartz plugs described previously, and then reflected through the lens in the camera box to the screen or photographic plate. The light reaching the glass screen is visible as a small bright spot. The distance from the screen or photographic plate to the external mirror, M, is equal to the distance from this mirror to the mirror inside the camera box plus the distance from the latter mirror to the pinhole, that is, the optical distances from the lens to the pinhole source and the screen were adjusted to equal the focal length of the lens. When the mirror, M, is moved by the expansion of the specimen or the temperature rod or both, the spot of light travels across the screen or photographic plate.

The back of the camera is provided with a hinged book form plate holder for 8 by 10 in. photographic plates or ground glass screen for photographic or visual observations, respectively.

III. CALIBRATION OF APPARATUS

After the apparatus was constructed and satisfactory temperature uniformity in the furnace was attained, 6 expansion tests were made with this apparatus on materials that had previously been tested with the Bureau's precision expansion apparatus, in order to calibrate the autographic expansion apparatus.

Figure 9 and table 1 show the observations obtained with the autographic apparatus on a 150 mm sample of copper alloy (1334 B). In fig. 9, OX represents the temperature axis and OY the expansion

axis. The temperature axis, OX, was located by turning the screw in contact with the fused-quartz plug to the right of the temperature rod, and indicating on a sheet of paper attached to the ground glass plate the path (OX) of the spot of light from right to left.[7] In a similar manner the expansion axis, OY, was located by turning the screw in contact with the fused-quartz plug to the right of the sample and indicating on this sheet of paper the path (OY) of the spot of light from bottom to top. This procedure may be simplified slightly

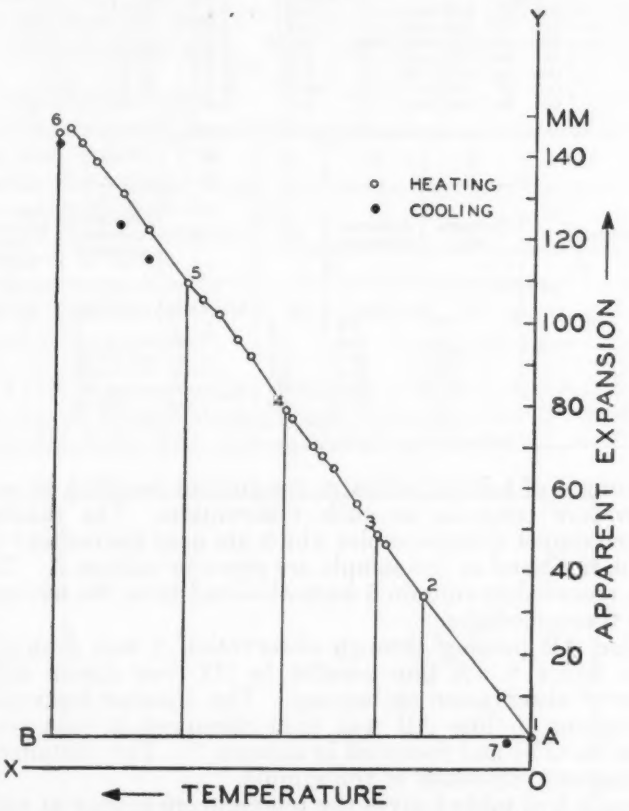

FIGURE 9.—*Observations on linear thermal expansion of copper alloy*

[The observer is located at the glass screen, G, of the camera box and is looking toward the furnace]

by indicating only points O, X, and Y before the test. Axes OX and OY may be drawn after the test has been completed.

The observations obtained on the sample of copper alloy (1334 B) are indicated in figure 10 and table 1. Observations 1 to 6 were obtained on heating and observation 7 was obtained after cooling to room temperature. At each of these observations the temperature was kept constant for a sufficiently long time to make certain that the sample had attained temperature equilibrium. The observations without numbers were taken without stopping to attain temperature equilibrium.

[7] The observer is located at the glass screen, G, of the camera box and is looking toward the furnace.

TABLE 1.—*Observations and computations on sample of copper alloy*

1	2	3	4	5				
Observation	Date	Time	Current	Thermocouple readings (millivolts)				
				Center	Left	Right	Center	Average
	1932		*Amperes*					
1	Oct. 13	3:34 p.m.	0.0	0.9	0.9	0.9	0.9	0.9
2	Oct. 14	8:42 a.m.	4.2	5.9	5.8	5.6	5.9	5.8
3	Oct. 14	11:32 a.m.	5.4	8.2	8.1	7.8	8.2	8.1
4	Oct. 14	1:35 p.m.	7.3	12.1	12.2	11.8	12.1	12.0
5	Oct. 14	2:43 p.m.	8.5	16.3	16.4	16.1	16.3	16.3
6	Oct. 14	3:35 p.m.	10.9	21.2	21.3	21.0	21.2	21.2
7	Oct. 15	9:05 a.m.	0.0	1.0	1.0	1.0	1.0	1.0

	6	7	8	9	10	11	12
Observation	Temperature	Apparent expansion	ΔT	$\Delta T \times 0.5$	Expansion in precision apparatus	Expansion in precision apparatus $-(\Delta T \times 0.5)$	M
	°C	*mm*	°C	*Millionths*	*Millionths*	*Millionths*	
1	22	0.0	0	0	0	0	
2	143	33.6	121	60	2,115	2,055	61.2
3	200	48.7	178	89	3,140	3,051	62.6
4	295	78.4	273	136	4,935	4,799	61.2
5	397	109.4	375	188	6,810	6,622	60.5
6	510	145.8	488	244	9,150	8,906	61.1
7	25						

Column 4 of table 1 indicates the current required to maintain the temperature constant at each observation. The readings of the chromel-alumel thermocouples which are near the center,[8] the left end and the right end of the sample are given in column 5. The temperatures recorded in column 6 were obtained from the average readings of the thermocouples.

A line AB passing through observation 1 was drawn parallel to OX in figure 9. A line parallel to OY was drawn through each numbered observation on heating. The distance from each of these observations to line AB was then measured in mm (along a line parallel to OY) and recorded in column 7. This distance represents the apparent expansion of the sample.

Column 8 of table 1 gives the temperature change at each observation from the initial temperature 22° C at observation 1. Column 9 indicates the expansion of the central portion (150 mm) of the fused quartz "stationary" axis. This expansion is equal to $\Delta T \times 0.5 \times 10^{-6}$. Column 10 gives the linear expansion obtained with the Bureau's precision apparatus on a duplicate sample (1334) from 22° C to the temperatures indicated in column 6. Column 11 indicates the differential expansion between the sample and the "stationary" axis. Each value in column 11 is equal to the difference between the corresponding values in columns 10 and 9.

The values for M in the last column of table 1 were obtained by dividing the values in column 11 by the corresponding values in column 7. M represents the constant or factor for this apparatus.

[8] Readings were repeated at the center, in order to give the center proper weight.

Additional values for M were obtained from the other 5 tests in a similar manner. All of the values for M obtained in the 6 tests are shown in figure 10. From these results, the average value for M represented by the horizontal line in the figure was found to equal 59.90 for temperatures between room temperature and about 700° C. This average value will be regarded as the best or final factor for this individual apparatus.

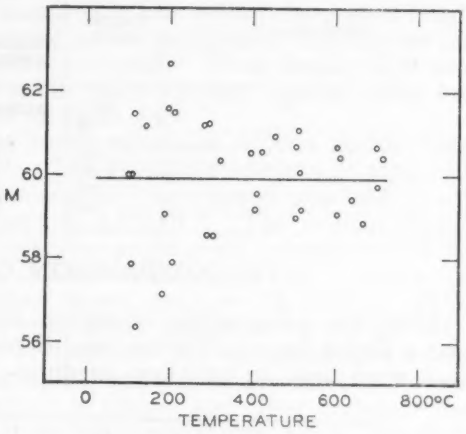

FIGURE 10.—*Values for M obtained in 6 tests*
Average value = 59.90

This factor (59.90) multiplied by the apparent expansion in mm (column 7 of table 1) plus the expansion of the central portion of the fused quartz "stationary" axis (column 9 of table 1), gives the linear expansion in millionths as determined by the autographic expansion apparatus on a 150 mm sample. Table 2 gives results obtained with this apparatus on the sample of copper alloy and also shows a comparison of these results with those obtained with the precision apparatus on a duplicate sample. Figure 11 shows a comparison of the expansion data plotted from the results given in table 2.

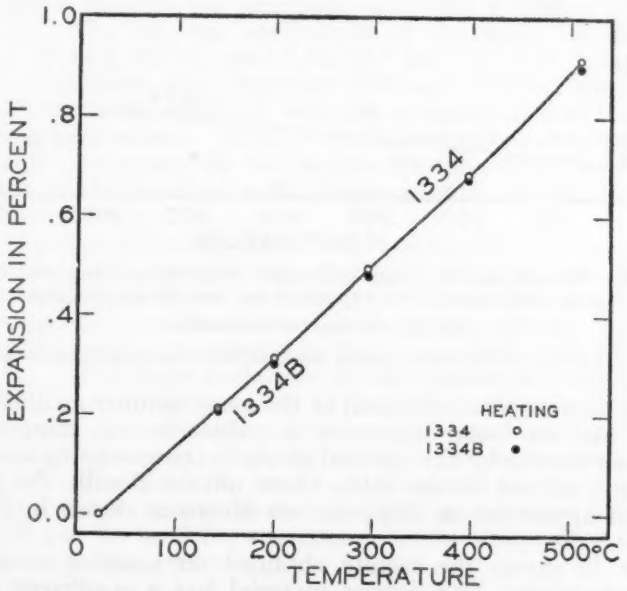

FIGURE 11.—*Comparison of expansion obtained on copper alloy with autographic apparatus and precision apparatus.*
1334—Precision apparatus; 1334B—Autographic apparatus.

TABLE 2.—*Comparison of expansion obtained on copper alloy with autographic apparatus and precision apparatus*

Observation	Temperature	Linear expansion		Deviation	Error
		Autographic apparatus	Precision apparatus		
	°C	*Millionths*	*Millionths*	*Millionths*	*Percent*
1	22	0	0		
2	143	2,072	2,115	43	2.0
3	200	3,006	3,140	134	4.3
4	295	4,832	4,935	103	2.1
5	397	6,741	6,810	69	1.0
6	510	8,977	9,150	173	1.9

IV. COMPARISON OF RESULTS

After the autographic expansion apparatus had been calibrated and a factor for equilibrium conditions had been derived, expansion tests were made on some low-, medium-, and high-expanding materials.

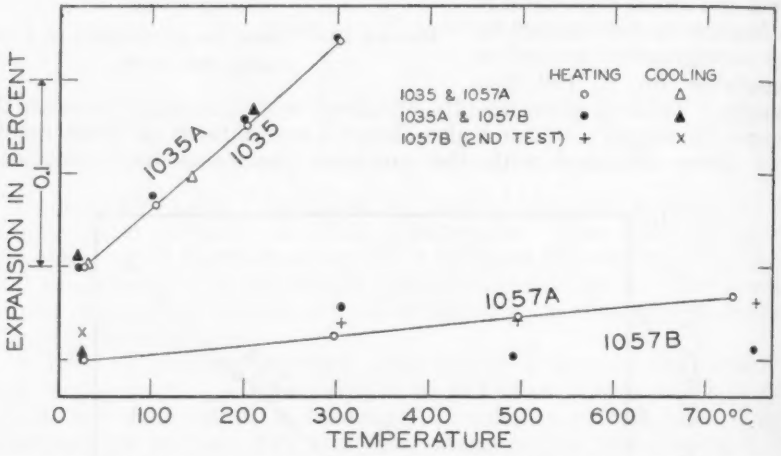

FIGURE 12.—*Comparison of linear expansion obtained on silica and borosilicate glass with autographic apparatus and precision apparatus.*

(All tests start from room temperature.)

1035 and 1057A—Precision apparatus; 1035A and 1057B—Autographic apparatus.

The observations were obtained in the same manner as illustrated in figure 9, and the linear expansion in millionths was computed from these observations by the method given in the preceding section. A comparison of the results with those obtained with the precision expansion apparatus on duplicate specimens is shown in figures 12 to 16.

Figure 12 shows the results obtained on samples of silica and borosilicate glass. The former material has a coefficient of linear expansion of 0.5×10^{-6} per degree C and the latter material approximately 4×10^{-6}. The agreement of the two types of apparatus is good for the glass, but it is not satisfactory for the fused silica. The

autographic expansion apparatus does not appear to be sufficiently sensitive for the most refined determinations of thermal expansion of materials having very low coefficients of expansion, such as silica and invar. In fact, for these materials, expansion apparatus having a high degree of accuracy is required. The actual changes in length for silica, invar, etc., as determined by the autographic method are just as accurate as those for any other material. When displayed on such a highly magnified scale as used in figure 12 they appear about four times greater than they would on figure 11.

The results obtained on the linear expansion of two thermometer glasses are shown in figure 13. The average coefficient of expansion of sample 1338 is 6.2×10^{-6} per degree C between 20 and 300° C, and for sample 1336 the coefficient is 8.2×10^{-6}. The critical regions located by the autographic apparatus are in good agreement with the critical regions located by the precision apparatus. Above the critical region, in the softening range, samples 1338B and 1336B tested by the autographic apparatus, indicated shrinkage. The shrinkage was caused by the pressure exerted on the samples in this method of test. The autographic apparatus appears to be well suited for locating critical regions of glasses and other materials that have transformations, but it is not satisfactory at temperatures where softening occurs.

Figure 14 shows the linear expansion of nickel-chromium-iron alloy and tempaloy. The average coefficient of expansion of the former alloy is 14.4×10^{-6} per degree C between 20 and 300° C and for the latter alloy the coefficient is 17.2×10^{-6}. The agreements in coefficients from the precision and autographic types are excellent.

Expansion data on an aluminum alloy and a bronze are given in figure 15. The average coefficients of expansion of these alloys between 20 and 300° C are 17.8×10^{-6} and 18.7×10^{-6}, respectively. For the aluminum alloy (samples 1206 and 1206A), the agreement between the results obtained with the autographic and the precision apparatus is excellent. Most of the observations obtained with the autographic apparatus on the bronze (sample 894A) are below the expansion curve obtained with the precision apparatus on the duplicate sample (894).

A comparison of the expansion curves obtained with the autographic and the precision apparatus on duplicate samples of a magnesium-aluminum alloy, is shown in figure 16. The broken or dashed curve representing the results obtained with the autographic apparatus is appreciably below the expansion curve obtained with the precision apparatus. The large deviations at the maximum temperature and on cooling to room temperature indicate that the sample bent [9] near the maximum temperature. It is well to point out here that the autographic apparatus should in many instances be employed with caution. It should not be used at high temperatures on magnesium alloys and other materials that deform at elevated temperatures. It should not be used for specimens which oxidize or fuse to fused quartz at high temperatures.[10]

[9] At high temperatures magnesium shows a tendency toward plastic flow. The tensile strength decreases rapidly with rising temperature.

[10] These temperatures may be determined by heating a small piece of the specimen, in contact with fused quartz, in a supplemental furnace.

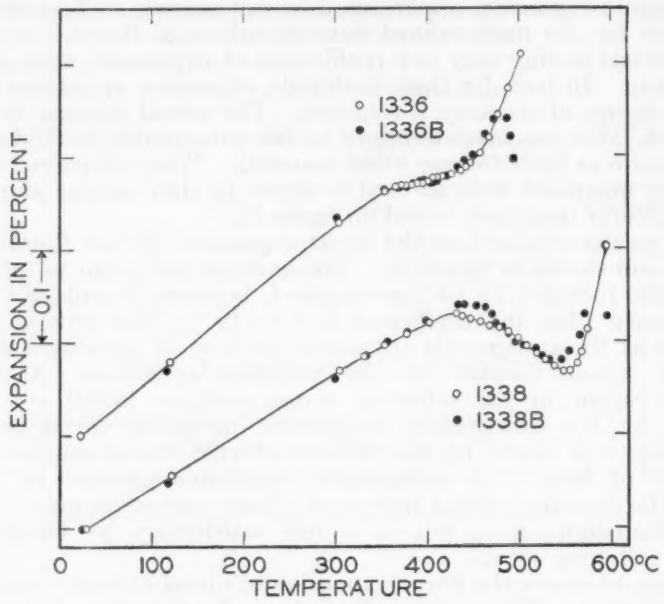

FIGURE 13.—*Comparison of linear expansion obtained on two thermometer glasses with autographic apparatus and precision apparatus.*

1336 and 1338—Precision apparatus; 1136B and 1338B—Autographic apparatus.

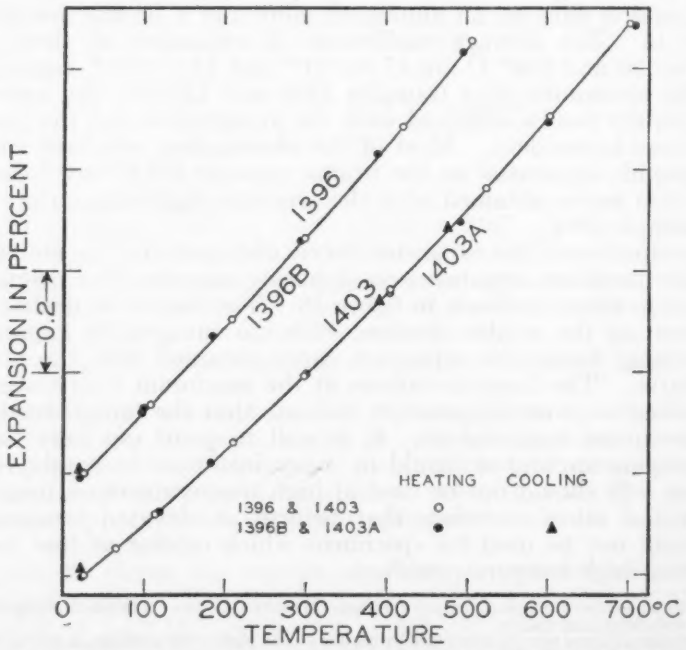

FIGURE 14.—*Comparison of linear expansion obtained on nickel-chromium-iron alloy (1403 and 1403A) and tempaloy (1396 and 1396B) with autographic apparatus and precision apparatus.*

1396 and 1403—Precision apparatus; 1396B and 1403A—Autographic apparatus.

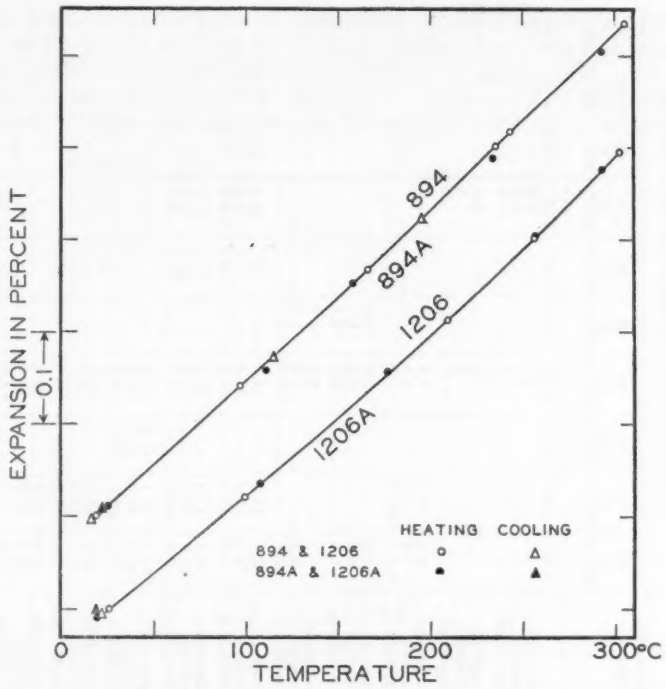

FIGURE 15.—*Comparison of linear expansion obtained on aluminum alloy (1206 and 1206A) and bronze (894 and 894A) with autographic apparatus and precision apparatus.*

894 and 1206—Precision apparatus; 894A and 1206A—Autographic apparatus.

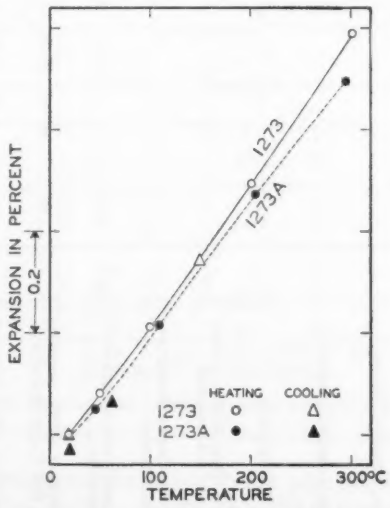

FIGURE 16.—*Comparison of linear expansion obtained on magnesium-aluminum alloy with autographic apparatus and precision apparatus.*

1273—Precision apparatus; 1273A—Autographic apparatus.

TABLE 3.—*Comparison of coefficients of expansion obtained with autographic and precision expansion apparatus*

Sample	Material	Chemical composition (per cent)						Expansion apparatus [1]	Average coefficients of expansion per degree centigrade									
		Iron	Silicon	Copper	Nickel	Manganese	Other elements		20 to 100° C	20 to 200° C	20 to 250° C	20 to 300° C	20 to 350° C	20 to 400° C	20 to 500° C	20 to 600° C	20 to 700° C	20 to 750° C
									×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶
1057B 1057A	Silica, annealed (1st test)							Autographic				1.0			0.0			+0.1
								Precision				0.5			+.5			+.5
								Deviation				+.5			−.5			−.4
1057B 1057A	Silica, annealed (2nd test)							Autographic				0.7			0.5			+0.4
								Precision				.5			.5			+.5
								Deviation				+.2			.0			−.1
1035A 1035	Borosilicate glass							Autographic	4.8	4.5		4.4						
								Precision	4.3	4.3		4.4						
								Deviation	+0.5	+0.2		0.0						
1338B 1338	Borosilicate thermometer glass,[2] not annealed							Autographic	5.2			5.9	6.0					
								Precision	6.2			6.2	6.1					
								Deviation	−1.0			−0.3	−0.1					
1336B 1336	Corning thermometer glass,[3] not annealed							Autographic	7.4			8.4	8.0					
								Precision	8.0			8.2	7.9					
								Deviation	−0.6			+0.2	+0.1					
1403A 1403	Nickel-chromium-iron alloy, hot-rolled	18.1	0.78		63.0	2.14	[4]	Autographic	13.4	14.3		14.5		14.7	15.0	15.6	15.9	
								Precision	13.4	14.0		14.4		14.8	15.2	15.7	16.0	
								Deviation	0.0	+0.3		+0.1		−0.1	−0.2	−0.1	−0.1	
1396B 1396	Tempaloy (soft), annealed at 850° C and quenched		.86	96.00	3.14			Autographic	16.8	17.0		17.1		17.4	17.7			
								Precision	16.6	16.7		17.2		17.3	17.8			
								Deviation	+0.2	+0.3		−0.1		+0.1	−0.1			
1206A 1206	Aluminum alloy, annealed at 400° C	0.84	19.30	3.14	4.18	1.08		Autographic	16.5	17.1	17.4	17.9						
								Precision	16.6	17.0	17.3	17.8						
								Deviation	−0.1	+0.1	+0.1	+0.1						
894A 894	Bronze, cast in green sand			85.5 to 87.5			[5]	Autographic	17.0	18.1		18.4						
								Precision	18.1	18.3		18.7						
								Deviation	−1.1	−0.2		−0.3						
1273A 1273	Magnesium-aluminum alloy, extruded at 330° C	.026	0.008	0.008		0.00	[6]	Autographic	24.2	25.6		25.3						
								Precision	26.2	27.1		27.9						
								Deviation	−2.0	−1.5		−2.6						

[1] The deviation is the coefficient of expansion obtained with the autographic expansion apparatus minus the corresponding coefficient obtained with the precision expansion apparatus.
[2] Similar to Jena glass 59 III.
[3] Developed for use with equivalent of Jena glass 16 III.
[4] Chromium 15.9, carbon 0.08, and phosphorus 0.013 percent.
[5] Tin 10.5 to 11.5, zinc 2.0 to 3.0, maximum impurities 0.2 percent.
[6] Magnesium 93.70 and aluminum 6.26 percent.

Table 3 gives coefficients of expansion of all the samples indicated in figures 12 to 16, inclusive. These coefficients were obtained with the autographic and the precision expansion apparatus. The table also shows the deviations or differences between the coefficients of expansion. These deviations vary from 0.0×10^{-6} to $\pm\ 2.6\times10^{-6}$.

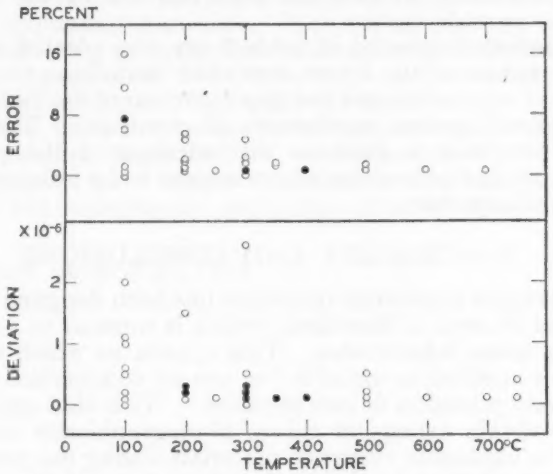

FIGURE 17.—*Deviations and errors for temperature ranges from 20° C to various temperatures indicated.*

Symbol: Black circle indicates more than one value.

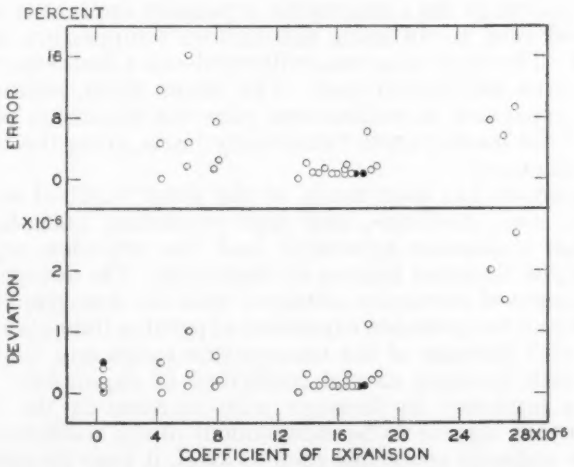

FIGURE 18.—*Deviations and errors against coefficients of expansion.*

Symbol: Black circle indicates more than one value.

The deviations indicated in table 3 are plotted in figure 17. The lower portion of the figure shows the deviations for temperature ranges from 20° to various temperatures between 100 and 750° C. The upper portion of the figure shows the errors [11] of the coefficients of

[11] The errors for sample 1057B (silica) were omitted.

expansion obtained with the autographic expansion apparatus for temperature ranges from 20° to various temperatures between 100 and 700° C. The errors were computed from the deviations on the assumption that the coefficients of expansion obtained with the precision expansion apparatus are correct. The deviations and the errors indicate a tendency to decrease with increase in the temperature range.

The deviations indicated in table 3 are also plotted in figure 18. The lower portion of the figure shows the deviations plotted against coefficients of expansion, and the upper portion of the figure shows the errors [12] plotted against coefficients of expansion. The deviations indicate a tendency to increase with increase of the coefficient of expansion, but the percentage errors appear to be independent of the coefficients of expansion.

V. SUMMARY AND CONCLUSIONS

An autographic expansion apparatus has been designed and built at the National Bureau of Standards, which is superior to a similar type used in European laboratories. This apparatus which employs the optical lever method is suitable for use in commercial laboratories where highest precision is not required. With this apparatus it is possible to obtain expansion curves photographically or to observe points on the expansion curves of materials during the progress of the test. The apparatus is useful for determinations of the linear expansion of various materials and also for locating transformation regions. A specimen 150 mm in length and from about 3 to 12 mm diameter is required.

A description of the autographic expansion apparatus is given, and the method used in obtaining satisfactory temperature uniformity is described. The apparatus was calibrated and a factor for this individual apparatus was determined. The factor 59.90, multiplied by the apparent expansion in millimeters, plus the expansion of the central portion of the fused-quartz "stationary" axis, gives the linear expansion in millionths.

A comparison has been made of the linear thermal expansion obtained on low-, medium-, and high-expanding materials with the autographic expansion apparatus and the precision expansion apparatus of the National Bureau of Standards. The deviations between the coefficients of expansion obtained with the autographic expansion apparatus and the precision expansion apparatus indicate a tendency to decrease with increase of the temperature range and they appear to increase with increase of the coefficient of expansion. The errors indicate a tendency to decrease with increase in the temperature range and they appear to be independent of the coefficients of expansion. For ordinary materials such as steel, it may be stated that the error of the autographic expansion apparatus is about 6 percent for the range from 20 to 100° C and about 3 percent for the range from 20 to 500° C.

The results show that the Bureau has accomplished the purpose indicated in the introduction of this paper. However, it should not be assumed that the autographic expansion apparatus is the best type for all laboratories. It does not give as accurate results as the fused-

[12] See footnote 11.

quartz expansion apparatus which was also designed for use in certain laboratories. Neither does the fused-quartz apparatus give results as accurate as the precision apparatus. Each type has its field of application.

The autographic expansion apparatus has its limitations and should be used with discretion. The apparatus is not sufficiently sensitive for tests on low-expanding materials. It is not satisfactory at temperatures where softening occurs in the specimen or for materials that bend at elevated temperatures. It is, however, a convenient, trustworthy, and efficient apparatus and fills a definite need.

Blueprints of both the fused-quartz expansion apparatus and the precision expansion apparatus are available and will be loaned to interested persons upon request. Detailed drawings for the construction of the autographic apparatus are not available at this date.

WASHINGTON, August 21, 1934.

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP723

Part of Journal of Research of the National Bureau of Standards, Volume 13, October 1934

A NOTE ON THE PURIFICATION OF α–*d*–XYLOSE AND ITS MUTAROTATION

By Horace S. Isbell

ABSTRACT

The method of purifying sugar solutions by treatment with basic lead acetate has been applied with excellent results to the purification of dark-colored xylose residues from cottonseed hulls. The sirup obtained after such treatment crystallizes during the evaporation and yields a practically colorless product of good keeping quality and high purity.

Mutarotation measurements on the purified product show that the reaction ate decreases during the first few minutes after solution.

In the preparation of xylose and other sugars from natural products the crude sugar is frequently contaminated with various gums and other substances which interfere with the crystallization. Although lead acetate has been widely used [1] in the clarification of raw sugars, its use has not been heretofore reported for the preparation of xylose from cottonseed hulls. As is well known, basic lead acetate forms difficultly soluble salts with nearly all the alpha hydroxy acids and with many complex substances. Unless these acids and complex substances are removed they are instrumental in inhibiting crystallization of the sugar, and frequently cause excessive foaming. When xylose is prepared from cottonseed hulls, dark-colored sirups are sometimes obtained from which it is difficult to separate a high-purity sugar. If the sugar solution is treated with basic lead acetate a nearly colorless sirup results, from which a pure product can be obtained in good yield. Crude xylose prepared from cottonseed hulls without the lead treatment frequently turns dark in a short time; the product obtained after the lead treatment usually remains colorless for a much longer time. The lead treatment removes impurities to such an extent that the sugar crystallizes readily during the evaporation so that it may be "grained" in the evaporation pan. It is thus possible to eliminate a large part of the time and expense that would otherwise be incurred in the growing of crystals in a crystallizer.

The amount of lead acetate used should be sufficient to precipitate the impurities without an unduly large loss of sugar; that is, the minimum amount required to give a light-colored sirup which can be evaporated without foaming. If desired, the excess lead can be removed from the sirups in one step with hydrogen sulphide. Removing the lead with phosphoric acid as described in this paper usually gives a slightly better clarification, but probably there is a larger loss

[1] Browne, Handbook of Sugar Analysis, p. 207. John Wiley & Sons, New York, 1912.

of sugar, as the phosphate precipitate is fine and difficult to wash free from sugar. Equally satisfactory results may be obtained by using either a solution of lead subacetate or dry lead subacetate. In some cases normal lead acetate will effect sufficient purification and it has the advantage that an excess does not cause a loss of sugar.

Ten kilos of crude xylose [2] containing considerable calcium sulphate, gums, and other impurities was dissolved in water and treated with 1 kg of decolorizing carbon and filtered. The volume of the filtrate was 16 liters and its density corresponded to 46.5 Brix. The dark-colored filtrate foamed badly because of the large amount of impurities present. After adding 1 kg of dry lead subacetate and 500 g of kieselguhr the sugar solution was filtered. The major part of the excess lead in the filtrate was precipitated by adding phosphoric acid (115 ml of 85 percent acid) until a faint purple reaction was obtained with Congo red paper. The lead phosphate was separated by filtration, using 500 g of kieselguhr. The lead remaining in the filtrate was removed by treatment with hydrogen sulphide, followed by another filtration using 100 g of decolorizing carbon. The lead-free filtrate which was nearly colorless was concentrated in vacuo. At about 60 Brix crystalline xylose began to separate; evaporation was continued until the solution contained about 73 percent of dry substance. The sirup containing considerable crystalline xylose was placed in a flask arranged so that it could be slowly rotated. After rotating overnight 3.3 kg of nearly pure xylose was separated by centrifuging. The mother liquor after evaporation gave an additional 3.4 kg of white crystalline sugar.

The same process was applied by the writer in cooperation with M. J. Proffitt, N. L. Bowman, P. E. Golden, and W. Pigman to the purification of a 139 kg batch of crude xylose. The sugar was dissolved in 259 kg of water and then treated with decolorizing carbon, lead subacetate, phosphoric acid, and hydrogen sulphide as described before. All operations were conducted with factory equipment. In this operation the crude xylose sirup after treatment with decolorizing carbon had a color index [3] of $-\log t=8.68$; after treatment with lead the color index dropped to $-\log t=0.02$. The sugar was crystallized in a copper evaporating pan, the temperature of which was held at about 40° C and the crystals grown in the manner used in refining sucrose.

The product was purified in glass containers by recrystallization from water according to the following procedure: 14 kg of the sugar was dissolved in boiling water (6 kg) containing about 200 g of decolorizing carbon, filtered, and placed in a flask which was rotated slowly for 2 days at room temperature. Large crystals formed which were separated on a centrifuge, washed with a small quantity of water, and dried in air. The first crop of crystals weighed 7 kg. The sirups were concentrated in vacuo to about 75 Brix and crystallized as before. By continuing the process nearly all the sugar was recovered.

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[2] The crude xylose was furnished by W. E. Emley, Chief of the Organic and Fibrous Materials Division of the National Bureau of Standards. It was part of the residues obtained from the xylose plant at the Anniston, Ala., plant of the Swann Corporation (Schreiber, Geib, Wingfield, and Acree, Ind. Eng. Chem. **22**,497(1930)). The purification of these residues by other methods has also been investigated by G. M. Kline and S. F. Acree of this Bureau.

[3] Peters and Phelps, Techn. Pap. BS **21**,261(1927);T338.

A 1.1000–g sample of α–*d*–xylose dissolved in water to make 25 ml, gave $[\alpha]_D^{20}=+89.2°$, 1.6 minutes after solution; +83.9°, 3.1 minutes; +78.7°, 4.9 minutes; +73.2°, 7 minutes; +65.0°, 10.4 minutes; +55.7°, 15 minutes; +48.0°, 20 minutes; +36.8°, 30 minutes; +27.1°, 45 minutes; +22.8°, 60 minutes; +20.0°, 90 minutes; +18.3°. 24 hours. The extrapolated initial rotation (graphically) is +94.8°. The mutarotation coefficients (k_1+k_2) calculated for these rotations are: 0.0225, 0.0211, 0.0206, 0.0206, 0.0207, 0 0205, 0.0205, 0.0209, 0.0205, and 0.0183. Although these results are in excellent agreement with the value [4] 0.0207, usually accepted for xylose at 20° C, attention is directed to the fact that the coefficient decreases slightly during the first few minutes. [5] This indicates that the mutarotation reaction which gives the constant 0.0207 is preceded by a more rapid reaction. This rapid reaction occurs whenever crystalline xylose is dissolved in water and will be discussed in a further publication relating to the products formed by the oxidation of the sugar with bromine water.

WASHINGTON, August 16, 1934.

[4] Int. Crit. Table, vol. 2 352.

[5] The importance of small deviations in the mutarotation coefficients has been emphasized by the results of Riiber, Lowry, and others who have shown the mutarotation reaction for many sugars is complex. See Kgl. Norske Videnskab. Selskabs Forh. 3, no. 17, 66(1930); and J. Phys. Chem. **33**,9(1929).

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP724

Part of Journal of Research of the National Bureau of Standards, Volume 13, October 1934

ACCELERATED TESTS OF NICKEL AND CHROMIUM PLATING ON STEEL

By Paul W. C. Strausser,[1] Abner Brenner, and William Blum

ABSTRACT

Plated specimens similar to those used in atmospheric exposure tests were subjected to accelerated tests, especially by means of a salt spray and by intermittent immersion in a salt solution. The time required for the first appearance of slight rust in these tests was not consistent and had no direct relation to the protective value of the coatings. When the extent of rust at the end of a definite period, for example 100 hours, was recorded, the results were approximately parallel to those of atmospheric exposure. The protective value of a metallic coating of this type depends principally upon its freedom from porosity. The latter can be determined in a few minutes by the ferroxyl test.

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I. INTRODUCTION

In a previous paper [2], the results of extensive exposure tests of nickel and chromium plating on steel were reported. That information is valuable in the selection and specification of the kind and thickness of plating for any given type of service. With adequate control and supervision, any given requirements for thickness can usually be met by a manufacturer or plater in his own plant. In such cases, however, it is desirable to have rapid methods of test to check the quality of the plating. Such tests are even more useful when parts are sent out to be plated, or plated parts are purchased, as then it

[1] Research Associate at the National Bureau of Standards for the American Electroplaters' Society.
[2] W. Blum, P. W. C. Strausser, and A. Brenner, J. Research NBS 13, 357 (1934); RP712.

is not usually practicable for the purchaser or user to check the time and current density employed in the plating operations.

The above exposure tests furnished a good opportunity to determine the relation between various accelerated tests and the behavior of the coatings under various atmospheric conditions. The specimens used in this investigation were a part of those plated for the exposure tests. They will be referred to by number, with sufficient description for their identification. For details of their preparation the previous paper should be consulted.

II. ACCELERATED CORROSION TESTS

The purpose of an accelerated corrosion test is to determine, in a short time, at least the relative value of different coatings under conditions likely to be encountered in service. The latter are, however, so varied that it is practically impossible to introduce all factors into an accelerated test, much less to control their relative effects. In general, therefore, it is preferable and customary to employ a simple test such as (a) exposure to a fine spray of sodium chloride, commonly known as a salt spray test, or (b) immersion in a corrosive solution, for example, intermittent immersion in a sodium chloride solution.

The principal substances that are likely to cause or accelerate corrosion of steel in the atmosphere are oxygen, water, carbon dioxide, sulphur dioxide and trioxide, and sodium chloride. The first three substances are always present, but generally their effects are slow and not directly susceptible of great acceleration. The sulphur compounds are found in urban and industrial atmospheres, and sodium chloride is present in marine exposures.

Various efforts have been made to introduce sulphur dioxide into simulated but accelerated atmospheric tests. The results here and elsewhere have shown that low concentrations of sulphur dioxide (0.1 to 1 percent), especially when continuously present, exert solvent effects on the coatings that are entirely unlike the effects of industrial atmospheres that contain fluctuating and much smaller concentrations of sulphur compounds. Sodium chloride has therefore been most extensively used in accelerated tests. It might be predicted, and has been approximately confirmed, that the results are at least similar to those obtained in a strictly marine exposure. The increased rate of corrosion is obtained partly by the use of high concentrations of sodium chloride and partly by the more severe conditions under which it is applied.

Another factor that can be varied to accelerate the corrosion is the temperature, which, however, should not be so high as to change the nature of the corrosion processes. As a temperature of 35° C (95° F) is often reached naturally, even in temperate climates, it was selected for use in the salt spray and intermittent immersion tests, which were carried out in a room with thermostatic control. Tests made at "room temperature" are subject to uncertainty through the fact that in uncontrolled rooms the extreme temperature at various seasons may range from 10° C (50° F) to 35° C (95° F). The latter temperature was selected because it is about the lowest that can be maintained throughout the year without artificial cooling.

Before applying any accelerated test to plated metals, the surface should be thoroughly cleaned in order to permit uniform access of the reagent to the surface. A simple test for cleanness is that the surface shall be uniformly wet with water, that is, there shall be no "water-break." The cleaning was accomplished in these tests by rubbing with cotton or cloth moistened with a thin paste of pure, fine magnesium oxide. Vapor cleaning with a suitable solvent is effective, but less convenient for laboratory testing.

1. METHODS

The salt spray and intermittent immersion were applied to most of the nickel and chromium finishes under the following conditions.

(a) SALT SPRAY

The salt spray test was conducted with a 20 percent solution of pure sodium chloride in a room kept at 35° C (95° F). The nozzle, air pressure, and baffle were so adjusted as to keep a uniform fine mist throughout the box and to wet uniformly the specimens, which were placed at an angle of 45° from horizontal. The solution that was condensed from the spray was drained off and not used again. The specimens with buffed nickel and chromium coatings were painted on the edges with a bituminous paint to prevent formation of rust there, which might run over the surface.

The specimens were inspected at the end of the first 6 hours and of each 24-hour period. At each inspection, they were washed lightly with running water and the number of rust spots on each specimen was noted. In addition, a rating of from 5 to 0, on the same basis as the exposure ratings, was given to each specimen. If, at the end of a definite period such as 100 hours, the corrosion was so pronounced that rust spread over the surface, the latter was cleaned by light rubbing with magnesium oxide paste, rinsed, and returned to the salt spray for 4 hours. This served to bring out the spots clearly without much spreading of the rust.

(b) INTERMITTENT IMMERSION

The intermittent immersion tests were also conducted with a 20 percent solution of sodium chloride. Each cycle included 1 minute in the solution and 14 minutes in air. The temperature was kept at 35° C (95° F) and the relative humidity at 60 ± 5 percent. This constant humidity insured a uniform tendency of the specimens to dry during the air exposures. Under these conditions they were visibly wet for about one-half the period in the air. The specimens were inspected at the same intervals as in the salt spray and the condition of each was similarly recorded.

2. RESULTS

The results of the accelerated tests may best be considered by comparing them with those of the atmospheric tests. The latter data in table 1 are based on 18 months' exposure. At Key West and Sandy Hook, the corrosion was more severe than at State College and Washington, and more easily rated than at New York and Pittsburgh.

TABLE 1.—*Porosity and accelerated tests on nickel and chromium finishes*

Set number	Total thickness	18 mo. atm ex. score			Ferroxyl Test Number of spots [1]	Salt spray				Intermittent immersion			
		KW SH	NY P	SC W		First rust	Spots at 100 hr [1]	Rating at 100 hr	Corresponding score	First rust	Spots at 100 hr	Rating at 100 hr	Corresponding score
	In.	*Percent*	*Percent*	*Percent*		*Hr.*			*Percent*	*Hr.*			*Percent*
(a) NICKEL													
52	0.00025	10	13	33	100	6	80	2	40	6	40	3	60
5	.0005	26	25	76	12	12	20	3.5	70	30	4	4	80
1	.001	65	52	87	3	20	5	4	80	30	2	4	80
6	.002	79	69	95	3	70	1	4.5	90	80	2	4.5	90
(b) NICKEL, COPPER, NICKEL													
53	.00025	4	13	15	200	6	100	1	20	6	100	1	20
15	.0005	13	3	81	40	6	70	2.5	50	25	35	3.5	70
13	.001	49	47	92	2	20	15	4	80	25	8	4	80
16	.002	69	65	99	0	6	10	4	80	75	2	4.5	90
(c) NICKEL, CHROMIUM													
152	.00025	9	20	51	80	15	100	2.5	50	50	35	3.5	70
105	.0005	10	20	72	20	25	25	3.7	70	65	2	4	80
101	.001	51	46	100	2	50	10	4	80	90	1	4.5	90
106	.002	80	84	96	0	55	1	4.5	90	85	0	4.5	90
(d) NICKEL, COPPER, NICKEL, CHROMIUM													
153	.00025	10	19	42	100	15	100	2	40	40	60	3	60
115	.0005	15	26	88	8	15	60	3	60	35	25	3.5	70
113	.001	36	39	98	2	15	20	4	80	40	25	3.5	70
116	.002	79	57	100	1	6	3	4.5	90	65	15	4.5	90

[1] Per specimen on 1 side, having an area of approximately 1.5 dm^2 or $\frac{1}{6}$ ft^2.

(a) SALT SPRAY

The results of this test are most commonly reported in terms of the period required for the initial appearance of rust. There is, however, considerable latitude in judging the amount of rust that constitutes failure in this test. Some define it as rust plainly visible at a distance of 3 feet. Others simply disregard what they consider to be very small rust areas. In this study, any rust visible to the unaided eye at a distance of 12 to 18 inches was recorded. The number of rust spots was noted at intervals, and a rating was was also given according to the scale used in the atmospheric tests.

The results in table 1 show that, as defined by us, the first appearance of rust has no direct relation to the quality of the coating. For example, in (b) and (d) a slight amount of rust appeared in 6 hours on very thick deposits (nos. 16 and 116), which were known to have good protective value in the atmosphere. The individual results are even more erratic than shown in table 1, which presents the averages of 3 specimens. It was not unusual for slight rust to appear on one specimen in 6 hours and on another of the same set in 50 or 100 hours.

If, however, the number of rust spots is recorded at the end of a definite period such as 100 hours, the results in the salt spray

are very similar to those of the ferroxyl test to be described later. Apparently, the salt spray merely detects pores, but requires 24 to 100 hours, instead of the 5 or 10 minutes required for the ferroxyl test. In general, the ratings at the end of 100 hours correspond inversely to the number of spots at that time. It is therefore suggested that in the salt-spray test greater attention be paid to the number and size of the spots after a definite interval than to the time of their initial appearance.

As the salt spray test is sometimes conducted with a dilute salt solution, and is almost always conducted without control of temperature, a few tests were made to determine the effects of concentration and temperature. The results, not recorded in table 1, may be summarized as follows:

With a *N* solution of sodium chloride (about 5.5 percent NaCl), the rate of failure of nickel and chromium plated steel was much slower than in a 20 percent solution. In general at 22° C (72° F) it required about 72 hours in the dilute solution to produce the same corrosion as appeared in 24 hours in the 20-percent solution.

The effect of temperature was more marked during the first part of the test period than during longer periods. For example at approximately 22° C (72° F) it required about 48 hours to produce the same corrosion as appeared in 24 hours at 35° C (95° F). However, at the end of 100 hours there was not much difference in the amount of rust produced at the 2 temperatures. It is apparent therefore that the customary definition of failure in terms of the time required for the first appearance of rust requires even closer control of temperature than when the extent of rust at the end of a longer period is estimated.

Any ratios based on the above tests are only approximate, and are useful merely for showing the direction and magnitudes involved, and not for making corrections for variations in temperature or concentration. Consistent results can be obtained only at a controlled temperature, for which 35° C (95° F) is the lowest practicable without artificial cooling.

(b) INTERMITTENT IMMERSION

The results of the intermittent immersion are very similar to those of exposure to salt spray and are subject to the same limitations. The periods for the first appearance of rust are somewhat longer, but more consistent than in the salt spray. The number of spots developed in 100 hours is usually less than in the salt spray. There does not appear to be any marked advantage in using the intermittent immersion test instead of the salt-spray test for nickel and chromium finishes.

(c) RELATION TO ATMOSPHERIC EXPOSURE

When the rating or number of spots after 100 hours is noted, both the salt spray and intermittent immersion tests place the sets of each group in the order of thickness, that is, in the same order of quality as in the atmosphere. They are therefore useful in distinguishing between good and poor coatings, even though the size, color, and distribution of the rust spots are not very similar to those in even a marine atmosphere, much less in an industrial atmosphere.

These two tests do not generally serve to detect small differences in protective value, which in turn are not usually consistent in different types of exposure. However, they both showed (in tests not recorded

in table 1) the superiority of nickel finishes applied over a buffed copper layer to those over unbuffed copper, which difference was also reported in the atmospheric tests. This effect was not observed when chromium was also present.

An example of misleading results in the salt spray and intermittent immersion tests is the fact that composite coatings of cadmium, copper, and nickel (set no. 25) failed very rapidly in both tests, but not in either a marine or an industrial atmosphere. When chromium was applied over the nickel (set no. 125), no marked failure of the composite coating was observed in either the accelerated or atmospheric tests.

III. POROSITY TESTS

Both the exposure tests and the accelerated tests showed clearly that the protective value on steel of coatings consisting of the more noble metals, such as copper, nickel, or chromium, depends almost entirely on their freedom from porosity, while that of less noble metals such as zinc and cadmium is approximately proportional to the minimum thickness. If it were possible to produce absolutely impervious coatings of the first group, especially of chromium, they would furnish permanent protection in most climates. Apparently the only practical method of approaching this goal is to make the deposits thicker, and even this method is not certain for chromium. Reliable tests for porosity may therefore be very useful for inspection, as they require much less time than the usual accelerated corrosion tests.

1. IN NICKEL COATINGS

(a) ON STEEL

Ferroxyl test.—This well-known test is applicable for detecting pores in any metallic coating on steel that is more noble than the steel. It depends upon treating the surface with a solution containing an agent, usually sodium chloride, that will attack steel but not the coating, and a substance that will react visibly with iron compounds. A ferricyanide solution is used, as it produces blue spots with any ferrous salt formed by the action of the sodium chloride on exposed steel. The mixed reagent may be applied as an aqueous solution, or one containing a gel (such as agar) that will form a congealed film, or in paper saturated with the reagent.[3] As the latter method yields a permanent record, it was employed in this investigation.

A study of this method showed that the concentration of the sodium chloride is not critical, though stronger solutions accelerate the attack of exposed steel. The concentration of ferricyanide should, however, be kept as low as possible and still yield blue spots. In high concentrations, the ferricyanide attacks nickel appreciably, especially in the presence of sodium chloride, and may therefore produce pores where the nickel is originally thin but not porous.

The most consistent results were obtained under the following conditions. The liquid reagent contained 60 g/l of sodium chloride and 0.5 g/l of potassium ferricyanide. For making the ferroxyl paper, 10 g/l of agar was dissolved in this warm reagent, and a 50 percent white rag bond paper was soaked in it and allowed to dry. The plated surface was cleaned by rubbing with fine magnesium oxide

[3] Pitschner, K., Proc. Am. Soc. Testing Materials [II], 27 304(1927).

and water, and rinsed, after which it was immersed in the ferroxyl solution without agar for 5 minutes. The paper was then moistened, pressed on the surface, and removed after 5 minutes. The number of blue spots, excluding those within 0.25 in. of the edge, was recorded.

As shown in table 1, when the ferroxyl test is applied to coatings consisting of copper, nickel, or chromium on steel, the porosity roughly corresponds (though inversely) to the thickness of the coatings and to their percentage scores in the exposure tests. The method serves to detect marked differences in porosity, such as are commonly observed on coatings of different thicknesses, but cannot be used to predict the small differences in behavior of specimens with the same thickness but with different composition. Just as with the above-described accelerated tests, it is difficult to incorporate the ferroxyl test into a specification because the value of the coating depends on the size of the pores as well as their number. The method is therefore chiefly of value for factory inspection of similar coatings and articles.

(b) ON COPPER

In most cases it is necessary to detect only those pores which extend through to the steel, which can usually be done with the ferroxyl test. Occasionally, however, it may be desirable to study the porosity of the separate layers, and especially of the outer nickel layer, in composite coatings that include a layer of copper.

Sometimes when the ferroxyl test is applied to composite coatings with an intermediate copper layer, red spots appear. These are caused by copper ferrocyanide, and their detection can be facilitated by adding a small amount, such as 1 g/l, of ferro-cyanide to the ferroxyl reagent.

Another method that yields fair results is to immerse the specimen in hydrogen sulphide water. Black spots appear where any appreciable area of copper is exposed, but fine pores are not readily detected.

(c) ON ZINC OR CADMIUM

It was found that by treating the surface for about 30 seconds with a solution that contained sulphuric acid (*N*, 49 g/l H_2SO_4) and copper sulphate (0.08 *N*, 10 g/l $CuSO_4.5H_2O$), copper deposited wherever zinc or cadmium was exposed. The presence of the copper was more readily detected by subsequently immersing the specimen in water saturated with hydrogen sulphide, which produced black spots. Any large pores or unplated areas were readily revealed, but the detection of fine pores was uncertain.

2. IN CHROMIUM

The methods for detecting pores or cracks in chromium coatings were fully described in a previous publication.[4] The copper deposition test, which depends upon the fact that copper is deposited only in pores or cracks in the chromium, was then found to be most reliable. When applied to various deposits used in this investigation, the results were consistent with those previously reported. This is important in view of the fact that some of the results of the exposure

[4] The porosity of electroplated chromium coatings, W. Blum, W. P. Barrows, and A. Brenner, BS J. Research **7**, 697(1931); RP368.

tests did not correspond with the predictions made on the basis of the porosity of the chromium coatings.

IV. CONCLUSIONS

Both the salt spray and intermittent immersion tests are useful for determining the relative quality, and especially the porosity, of coatings consisting of copper, nickel, and chromium. The results are more significant and more closely related to those of atmospheric exposure if the number and size of the rust spots at the end of a specified period, such as 100 hours, are recorded, rather than the time for the first appearance of rust. These methods do not, however, closely reproduce the types of corrosion produced in the atmosphere, and do not serve to detect small differences in protective value. The ferroxyl test is a rapid, reliable method for determining the relative porosity of the coatings.

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INFLUENCE OF CHEMICALLY AND MECHANICALLY FORMED NOTCHES ON FATIGUE OF METALS

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ABSTRACT

An introductory section discusses the importance of stress concentration due to notches, as a cause of failures in service. Resistance of a notched specimen to fatigue and to impact may depend on entirely different properties. This paper considers the influence of notches on fatigue.

Section II considers the effect of chemically formed notches, attention being confined to the influence of pitting caused by stressless corrosion. Relationship between tensile strength and the percentage decrease in the fatigue limit for steels and aluminum alloys is illustrated by composite curves. Each of these curves is presumed to represent this relationship for a notch of fairly constant effective sharpness. The three-dimensional relationship between corrosion time, percentage damage, and tensile strength is illustrated and discussed.

The general object of section III is to determine whether composite curves of similar form may be obtained by a study of experimental data obtained by a number of investigators with mechanically formed notches. The fact that such graphs have been obtained, each representing the influence of one form of notch on one kind of metal, confirms the conclusion that a stressless corrosion graph of this type represents the influence of a notch of fairly constant effective sharpness. Reasons are discussed for the deviation of individual results from the ideal composite curve for a mechanically formed notch.

Section IV considers the relationship between notch sensitivity (as measured by percentage damage) and other properties of metals. The properties considered are: Hysteresis, ductility, and work-hardening capacity. Evidence is presented that scatter of individual results in a composite graph, of the type used, is due largely to differences in tensile work-hardening capacity. Evidence is also presented that notch sensitivity, while depending somewhat on elastic hysteresis, depends largely on work-hardening capacity.

Section V considers the influence of notches in diminishing the advantage of superior strength.

Section VI is a list of the selected references cited in the text.

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I. INTRODUCTION

The importance of stress concentration does not need emphasis to anyone who has examined a number of failed parts of structures and machines. In a collection of a number of failed shafts of naval vessels, for example, it was observed that the fracture invariably had started at a radial hole, such as an oil hole or screw hole. In any other collection of failed machinery parts, it would be found that fracture in each case had started in some region of stress concentration, such as a hole, thread, key way, notch, corroded surface, or some other region of abrupt change of section. This does not necessarily mean that such abrupt changes of section are in every case the chief cause of failure. It does mean, however, that these regions are sources of weakness, are at least contributory causes of failure, and in many instances the chief cause.

Designers, manufacturers, and users frequently do not realize the importance of such regions of stress concentration. If a hole, groove,

[2] Figures in parentheses here and throughout the text indicate references given in the list at the end of this paper.

keyway, or corrosion pit causes little reduction in cross section, the resultant loss of strength frequently is considered of little importance. This erroneous impression often is due to lack of knowledge of the entire subject of stress concentration. Even those who have some knowledge of theoretical stress concentration, however, often minimize its practical importance because of the fact that it is not usually important when the loading is static.

Under static loading, regions of high stress concentration are of only slight importance, unless the metal is brittle. Such regions usually are very small in comparison with the entire area of cross section. If, therefore, the metal is even moderately ductile, it merely yields slightly in regions of highest stress, with resultant partial relief of the stress concentration, and with practically no weakening of the entire structure or machinery part. The great majority of failures of machinery parts and some of the failures of structural parts, however, are due to many repetitions of a stress range. Under these conditions, the influence of holes, grooves, and other abrupt changes of section is of great importance. Such discontinuities lower the fatigue limit.

To save space, there is need for a single word as a general designation for all discontinuities, whether they be holes, notches, grooves or other depressions. For this purpose, the word "notch" will hereafter be used, a hole being considered as an internal notch.

Resistance of a notched specimen to fatigue and to impact may depend on entirely different physical properties. The properties of many machinery parts should be such as to give resistance to both fatigue and impact. In this paper, however, attention will be confined to the effect of notches on fatigue.

II. INFLUENCE OF CHEMICALLY FORMED NOTCHES ON FATIGUE OF METALS

1. INFLUENCE OF PRIOR STRESSLESS CORROSION ON THE STRESS-CYCLE GRAPH

In the course of an investigation of the combined influence of stress and corrosion, one of the authors has accumulated considerable data on the influence of prior stressless corrosion on fatigue. Recent correlation of the data has shown that the results are applicable to a study of the influence of notches on fatigue of metals. The use of chemically rather than mechanically formed notches in such a study, moreover, has some advantages, which will become apparent.

Investigation of the damaging effect of corrosion is essentially investigation of the effect of chemically formed notches. The effect of corrosion usually is due less to general loss of section than to stress concentration caused by corrosion pits. In considering the effect of corrosion pits, attention will here be confined to the influence of prior stressless corrosion. The influence of simultaneous stress and corrosion (stress corrosion or "corrosion fatigue") will not be considered.

Typical graphs [3] illustrating the influence of prior stressless corrosion on fatigue of carbon steels and ordinary alloy steels are shown in

[3] The word "graph" in this paper is used to denote all the graphical data relative to a single line or curve. The word includes in its meaning all the individual experimental points as well as the established line or curve. The word "diagram" is used to denote a series of graphs in the same figure.

figure 1. These are ordinary stress-cycle graphs redrawn on a more open scale from a figure in a previous paper by one of the authors (22). The 3 groups of graphs represent results obtained with a chrome-vanadium steel that had received 3 different heat treatments. The chemical composition of this steel (AZ) is given in table 1, details of heat treatment are given in table 2, and physical properties are given in table 3. The rotating-cantilever specimens used were of the tapered form described in previous papers by one of the authors (17, 18).

The uppermost curve in each group was obtained with uncorroded specimens. The other curves were obtained with specimens previously corroded in water for the times indicated at the right of the curves. The water used in these experiments was an ordinary well water, which was used extensively in previously described experiments by one of the authors (21, 22). As this water contained considerable calcium carbonate, it will hereafter be designated "carbonate water." After stressless corrosion for the indicated times in a stream of water, the specimens were dried, oiled, and subjected to fatigue tests, with the results illustrated in the figure.

The curves for previously corroded specimens, like the curves for uncorroded specimens, approach a horizontal asymptote. The lower part of each curve representing corroded specimens is approximately parallel to the curve representing uncorroded specimens. Because of this parallelism, only 1 or 2 specimens need be tested to establish the lower part of a curve, provided the specimens do not break at much less than a million cycles.

The greater the prior corrosion time, as illustrated in figure 1, the greater is the vertical distance between the curves representing corroded and uncorroded specimens. The lowering of the curve with increasing corrosion time is due to increasing stress concentration caused by increasing depth of corrosion pits.

The fatigue limit, which is the highest (nominal) cyclic stress that the specimen will endure without eventual failure, is represented by the ordinate of the horizontal asymptote of the stress-cycle curve. For steels, this limit is represented with sufficient accuracy by the ordinate of the curve at 10 million cycles. The lowering of the fatigue limit due to pitting may be used as a measure of the damage.

2. DECREASE IN THE FATIGUE LIMIT WITH CORROSION TIME

A useful type of graph may be obtained by plotting corrosion times against resultant fatigue limits. Examples of this type of graph, assembled from previous papers by one of the authors, are given in figure 2. Each curve in this figure represents the influence of time of prior stressless corrosion on the fatigue limit of a steel or other alloy. The ordinate of the origin of each curve represents the fatigue limit of the uncorroded alloy (endurance limit). The course of each curve represents the lowering of the fatigue limit with increasing corrosion time.

One of the curves represents stainless iron, 2 curves represent aluminum alloys, and the remainder represent carbon steels or ordinary alloy steels. Chemical compositions are given in table 1, details of heat treatment are given in table 2, and tensile properties are given in table 3. Unless otherwise stated, corrosion was in carbonate water at room temperature.

The curves for ordinary steels and for aluminum alloys are of the same general form. As illustrated by these curves, the rate of damage at first is rapid, but decreases with increasing corrosion time, and eventually becomes very slow. As illustrated by the group at the right of figure 2, the rates of damage in steam boiler water and in cool distilled water are less than in cool carbonate water. The relatively low rate of damage in boiler water (in spite of the high temperature) is due to low concentration of dissolved oxygen. The low rate in distilled water is due to low concentration of dissolved salts. Variables other than corrosion time evidently may influence greatly the rate of damage due to corrosion.

The behavior of alloys relatively resistant to corrosion is illustrated by the curve for stainless iron, JB–W–12. For a considerable time in contact with water the fatigue limit of this alloy is practically unaffected. Eventually, however, the fatigue limit begins to decrease, and falls at an increasing rate. Similar curves may be obtained with nickel, Monel metal, aluminum bronze, etc. A curve of this form has been called an "accelerated damage" curve. All the curves in figure 2 excepting the curve for stainless iron may be called "retarded damage" curves.

3. PERCENTAGE DAMAGE DUE TO CORROSION: RELATIONSHIP BETWEEN PERCENTAGE DAMAGE AND TENSILE STRENGTH

Because of the wide variation in physical properties of the metals, the stressless corrosion curves in figure 2 differ greatly in position and slope. For better comparison of the effects of corrosion on such widely differing metals, it is convenient to use another type of diagram, in which decreases in fatigue limit are expressed as percentages of the endurance limit. (By endurance limit is meant the fatigue limit obtained with smooth, uncorroded specimens.) By means of diagrams of this type, a study has recently been made of data obtained by stressless corrosion of a great variety of alloys in carbonate water. The experiments were made by one of the authors while at the U.S. Naval Engineering Experiment Station, Annapolis, Maryland. Results thus obtained have been published in various papers, but have not previously been studied with reference to percentage damage. Recent study of the data has shown that composite graphs may be constructed to represent relationship between percentage damage and tensile strength.

4. COMPOSITE GRAPHS FOR CARBON STEELS AND ORDINARY ALLOY STEELS

Composite graphs representing corrosion of carbon steels and ordinary alloy steels in carbonate water are shown in figures 3 and 4. Each symbol shown in the figures represents a result obtained with a steel of the indicated composition; each graph represents the damaging effect of corrosion for the indicated constant time. The curves have been drawn so as to give due weight to each experimental point. In view of the evident convergence of some of the curves toward the origin of coordinates, and for theoretical reasons, all the curves have been drawn so as to converge toward this same point. Such convergence being assumed, the approximate form and position of each curve are fairly well established. Moreover, the assembled curves, as shown in figure 4, form a consistent series.

The 10-day corrosion curve is best established. The scatter of experimental points for this graph varies with the strength of the steels. For the alloy steels with tensile strength greater than 120,000 lb, the scatter of experimental points is surprisingly small. For the steels with lower tensile strength, and especially for the carbon steels, the scatter is considerably greater. Wide scatter, however, is confined to only 5 of the 24 experimental points. Similar increase in scatter with decrease in tensile strength is found in the 25-day graph of figure 4 and the 50-day graph of figure 3. It is not surprising that scatter is greater for low-strength than for high-strength steels, because the experimental error in determination of the damage (difference between the fatigue limits of corroded and uncorroded specimens) increases with decrease in the tensile strength. For example, an error of only 1,000 lb/in.^{2} in determination of the fatigue limit of a soft steel might cause an error of more than one-fourth the estimated percentage damage. Although ordinary experimental errors may account for part of the scatter, however, a large part probably is due to another variable which will be discussed later.

These curves are believed to represent the average relationship between tensile strength and percentage decrease in the fatigue limit, due to constant corrosion intensity and constant time. The evidence seems to indicate that percentage damage depends largely on tensile strength. The rate of change of percentage damage with strength is large for low-strength steels, but decreases with increase in tensile strength. As Brinell hardness is approximately proportional to tensile strength, similar curves could be drawn to represent relationship between Brinell hardness and percentage damage.

The fact that pitting of carbon steels and ordinary alloy steels in water depends very little on composition or physical properties suggests the idea that each composite graph in figures 3 and 4 probably represents the influence of pits of nearly constant effective sharpness.[4] On this assumption, each curve would represent the increasing effect of a fairly constant notch with increase in tensile strength. (That this assumption is approximately correct is confirmed in section III by comparison of the curves representing stressless corrosion with curves representing mechanically formed notches.) Such curves, as they extend to the right, probably approach a horizontal asymptote, at an ordinate which may or may not correspond to the theoretical stress concentration factor.

5. THREE-DIMENSIONAL RELATIONSHIP BETWEEN CORROSION TIME, PERCENTAGE DECREASE IN FATIGUE LIMIT, AND TENSILE STRENGTH, FOR CARBON STEELS AND ORDINARY ALLOY STEELS

The assembled curves at the right of figure 4 illustrate, by their relative positions, the relatively great effect of the first few days' corrosion time and the gradually decreasing rate of damage with increase in corrosion time. Corrosion for 3 days evidently causes about half as much percentage damage as corrosion for 50 days, Corrosion for 10 days causes about five-sixths as much damage as corrosion for 50 days.

[4] The "effective sharpness" or "equivalent sharpness" of a notch depends not only on depth and radius of curvature, but also on relative and absolute size. The effect of a very small notch, for example, may be considerably less than that of a large notch with the same ratio of depth to radius of curvature. The effect of a corrosion pit, the refore, may depend more on the general shape than on the sharpness of minute salients.

The influence of corrosion time is better illustrated by the composite diagram in figure 5, which was developed from the diagram at the right of figure 4. Each curve in figure 5 represents the influence of corrosion time on percentage damage for steels having the indicated tensile strength. The form of each curve illustrates the initial rapid rate of damage and the gradual decrease in rate with time.

As the ordinate scales for the diagram in figure 5 and the diagram at the right of figure 4 are the same, these diagrams may be considered as two views of coordinate lines on a three-dimensional diagram. The top or plan view of this diagram is shown in figure 6. The curves in this figure may be considered as contour lines on a three-dimensional diagram. Each curve represents the relationship between tensile strength and corrosion time for the indicated constant percentage damage. For tensile strengths above about 180,000 lb the diagram is based on extrapolation of the diagrams in figures 4 and 5. The extrapolated portion of the diagram, however, is qualitatively, and probably not far from quantitatively, correct.

As illustrated by the course of the curves in figure 6, the corrosion time required to cause constant percentage damage decreases greatly with increase in tensile strength. The time required to cause 15-percent damage, for example, decreases from about 60 days to less than 1 day as the tensile strength is increased from 40,000 to 260,000 lb. The time required to cause 40-percent damage decreases from about 80 to 5 days as the tensile strength is increased from 120,000 to 260,000 lb. This diagram, therefore, illustrates the great importance of protecting steels of spring temper against the effect of even brief corrosion.

A contour line on the three-dimensional diagram does not represent constant effective sharpness of pitting. Constant effective sharpness of pitting is represented by a constant-time curve of the type shown in figures 3 and 4.

6. INFLUENCE OF PRIOR STRESSLESS CORROSION ON THE FATIGUE LIMIT OF ALUMINUM ALLOYS

Results of corrosion experiments with aluminum alloys are shown in figure 3 in comparison with results obtained with steels. The curves, drawn from the origin of coordinates so as to give due weight to each experimental point, are similar in form to the curves for steels. As shown by the relative positions of the curves, the percentage damage caused by 10 days' corrosion is more than half as great as the percentage damage caused by 50 or 100 days' corrosion. This time-damage relationship is in accordance with the form of the curve for aluminum alloys in figure 2. As there shown, the rate of damage is rapid at first, but gradually decreases, and after about 50 days is very slow.

The composite curves, drawn to represent the 10-, 50-, and 100-day results, apply properly only to the alloys that have not been cold-worked. As will be shown later, metals strengthened by cold working and metals strengthened by heat treatment, probably should not be represented by the same composite graph. The composite curves for aluminum alloys, like the composite curves for steels in figures 3 and 4, are intended to represent the effect of variation of tensile strength due to composition and heat treatment, not to cold working.

Most of the results for cold-worked aluminum and aluminum-manganese alloys, however, fall within the range of scatter of these graphs.

The 10-day curve for aluminum alloys, as illustrated in figures 3 and 4, is considerably above the 10-day curve for steels, and is even above the 200-day curve for steels. The 50-day curve for aluminum alloys is far above the 50-day curve for steels. Percentage damage due to corrosion, therefore, is considerably greater for aluminum alloys than for steels of the same tensile strength.

Each composite curve, for aluminum alloys as for steels, probably represents the influence of corrosion pits of practically constant effective sharpness. The slope of each curve, therefore, probably represents the increase in notch effect with tensile strength. (Notch effect for fatigue alone is under consideration.) The fact that the slopes of the curves are steeper for aluminum alloys than for steels could be due to either or both of two causes: (a) Greater effective sharpness of pitting in aluminum alloys than in steels; (b) greater notch sensitivity of aluminum alloys. Evidence presented in the following sections throws some light on the relative importance of these two factors.

III. INFLUENCE OF MECHANICALLY FORMED NOTCHES ON FATIGUE OF VARIOUS METALS AND ALLOYS

1. EFFECT OF A NOTCH ON THE FATIGUE LIMIT OF STEELS: DATA OF ONE OF THE AUTHORS

If each composite curve in figures 3 and 4 represents the influence of chemically formed notches of practically constant effective sharpness, curves of similar form should be obtainable by use of mechanically formed notches. Very little investigation of the effect of notches however, has been done in such a way as to supply the needed data. There have been some important investigations of the effect of notches of various sizes and shapes, with use of one or several alloys. But there has been very little investigation of the effect of notches of the same size and shape on metals having a wide range of composition and physical properties. The published results of investigation, moreover, are not easily evaluated, because the effect of a mechanically formed notch is influenced by several important variables. Perhaps the most important of these variables is the influence of the notch-forming process on the surrounding metal. A study of published data has been made however, on the basis of the relationship illustrated by the curves for chemically formed notches.

Results of previous experiments, made by one of the authors, have been found to throw some light on this subject. Most of these results have been presented in a previous paper (21) in the form of stress-cycle graphs. Percentage damage and its relation to physical properties, however, were not studied at that time. The experiments consisted in fatigue tests of notched and unnotched rotating-cantilever specimens. The notch was of the form and dimensions shown in figure 7. Special care was taken in the machining, and the radius of curvature at the bottom of the notch was checked microscopically.

Results obtained with carbon steels and ordinary alloy steels are represented in figure 7. The composition of each of the steels is given in table 1, details of heat treatment are given in table 2, and physical

properties are given in table 3. The numeral adjacent to each plotted symbol refers to the corresponding numeral in the first column of table 3.

A composite curve has been drawn so as to give due weight to each experimental point. Although these points are few and rather widely scattered, the evidence seems to indicate that the composite curve is similar in form to the curves obtained with chemically formed notches. The curve apparently points toward the origin of coordinates and, as it extends to the right, probably approaches a horizontal asymptote. The damaging effect of a mechanically formed notch evidently increases with the tensile strength, but at a gradually decreasing rate.

The horizontal asymptote may or may not represent, by its position, the theoretical percentage damage due to a notch of this form and relative size. As the notch used was rather large in relation to the diameter of the specimen, the theoretical percentage damage (based on the nominal stress in the minimum section) would be somewhat smaller than the theoretical percentage damage due to a relatively small notch. For a relatively small notch of this form, the theoretical stress concentration factor $\left(1+2\sqrt{\frac{d}{r}}\right)$ would be 11.6 and the theoretical percentage damage would be 91.4. The horizontal asymptote in figure 7, however, has been placed at a somewhat lower percentage, estimated from data on the effect of the same notch on copper.

2. EFFECT OF A NOTCH ON THE FATIGUE LIMIT OF COPPER: DATA OF ONE OF THE AUTHORS

The effect of a notch on the fatigue limit of copper is illustrated by the graph at the left of figure 7. This graph is based on results of experiments published in a previous paper by one of the authors (21). (In that paper, percentage damage and its relationship to physical properties were not considered.) The form and dimensions of the notch used are shown in the figure.

The lower of the two experimental points represents fully annealed material; the upper point represents cold-worked material. The relatively high positions of these two points seem to indicate that notch sensitivity of copper is high. Even for annealed copper, notch sensitivity evidently is equal to that of steels with tensile strength five times as great.

The curve has been drawn through the two experimental points and to the origin of abscissas. It has also been drawn so as to become practically horizontal at an abscissa corresponding to the "true-breaking stress", 76,000. (Reasons for so drawing the curve will be considered later.) The ordinate for this point may correspond to the theoretical percentage damage for a notch of this form and relative size, or to somewhat less than the theoretical percentage. The asymptote of the curve, however, evidently should be at a higher percentage than 76, the experimental value indicated in figure 7 for cold-worked copper. The asymptote should also be at a lower percentage than 91.4, the theoretical value for a relatively small notch. A percentage midway between these two values has been arbitrarily selected.

3. EFFECT OF A NOTCH ON THE FATIGUE LIMIT OF NICKEL-COPPER ALLOYS: DATA OF ONE OF THE AUTHORS (21)

The effect of a notch on the fatigue limit of nickel-copper alloys is illustrated by the graph at the right of figure 7. The notch used in investigation of nickel-copper alloys was the same in form and size as the notch used in investigation of steels and copper. The nickel-copper alloys represented in the figure range in composition from 21 percent nickel to commercially pure nickel. Some of the alloys were fully annealed; others were in work-hardened condition.

The same composite graph probably should not be used to represent both a range of properties due to variation in the degree of cold working and a range due to variation in composition and heat treatment. For this reason, no attempt has been made to draw a composite curve in figure 7 to represent the nickel-copper alloys. For comparison of positions, however, the composite curve for steels has been reproduced. By such comparison, in spite of the meagerness of the data and only approximate determination of some of the experimental points, it is possible to draw some conclusions about the notch sensitivity of these alloys.

For moderately work-hardened nickel and Monel metal, and for a slightly work-hardened alloy containing 40 percent nickel, notch-sensitivity evidently is about the same as for steels (not cold worked). For the alloys having 21 and 29 percent nickel, either annealed or moderately cold worked, notch sensitivity possibly is somewhat less than for steels.

4. EFFECT OF A NOTCH ON THE FATIGUE LIMIT OF STEELS: DATA OF HOUDREMONT AND MAILANDER

The effect of a small sharp notch on the fatigue limit of a number of steels with wide range of composition and physical properties has been investigated by Houdremont and Mailander (10). The notch used in their experiments was 0.1 mm deep and "as sharp as possible". No information, therefore, is available as to the ratio of depth of notch to radius of curvature. No clear information, moreover, is available in regard to the method of forming this notch.

Results of their experiments were represented in their paper by a diagram with coordinates similar to those in figures 3 and 7. The curves in their diagram, however, increase in slope with increase in tensile strength. Such curvature is not in accordance with theory, and is not an essential representation of their data. The results of their experiments, therefore, have been replotted and a composite curve has been drawn so as to approach the origin of coordinates and also to approach a horizontal asymptote. This graph is shown in figure 8, together with a miscellaneous collection of graphs representing results of experiments by a number of investigators, to determine the effect of notches, fillets, keyways, depressions, and surface roughness.

The curve representing results obtained by Houdremont and Mailander, drawn so as to give due weight to each experimental point, is almost identical with the 200-day corrosion curve, figures 3 and 4. Moreover, the scatter of experimental points in this graph, as in the graphs of figures 3 and 4, decreases with increase in tensile strength. In the group of points representing tensile strength be-

tween about 163,000 and 180,000 lb, which includes steels of various compositions and heat treatments, the scatter is surprisingly small. The scatter in such graphs, as previously stated, probably is due in part to the influence of another variable which will be discussed later.

Results obtained with austenitic steels, not shown in the figure, seem to indicate that mechanically formed notches cause much less percentage damage to austenitic steels than to carbon steels or ordinary alloy steels. A similar conclusion has been reached by Ludwik (14). Possible reasons for lower notch sensitivity of austenitic steels will be given later.

5. INFLUENCE OF A NOTCH ON THE FATIGUE LIMIT OF STEELS: DATA OF H. F. MOORE AND S. W. LYON

Results of experiments by H. F. Moore and S. W. Lyon (24) are shown in figure 9 (A). These authors used a rotating beam specimen with a groove of semicircular cross section. The steels used had a wide range of composition and physical properties. Because of the small number and wide scatter of experimental points, it is not possible to draw a composite curve on the basis of these points alone. For comparison, however, the 10-day corrosion curve in figure 3 has been reproduced in figure 9 (A). The position of the experimental points with reference to this curve is such as to indicate that an ideal curve based on a larger number of points probably would not differ greatly from the 10-day corrosion curve.

6. EFFECT OF A NOTCH ON THE FATIGUE LIMIT OF STEELS: DATA OF LUDWIK AND SCHEU

Results of experiments with a great variety of steels by P. Ludwik and R. Scheu (12,13,14) are represented in figure 9 (B). The diameter of the specimen was 9.5 mm; the notch was 0.2 mm deep, with root radius 0.05 mm.

The experimental points shown in the figure are widely scattered. The scatter decreases with increase in tensile strength, however, as in the graphs shown in figures 3, 4, 7, and 8. For comparison, the curves representing effects of 10, 25, 50, and 200 days' corrosion, established in figures 3 and 4, have been reproduced in figure 9 (B). Between the 10-day and 200-day curves are included 18 of the 25 experimental points; another point is only slightly below the 10-day curve. The remaining 6 points, which are considerably below the 10-day curve, are separated by a wide gap from the other 19. Results obtained by Ludwik and Scheu, therefore, are not in accord with results obtained by Houdremont and Mailander, as represented in figure 8, or with data in figures 3, 4, and 7. The data in figure 9 (B) apparently do not indicate a definite relationship between notch sensitivity and tensile strength.

It seems probable, however, that the positions of some, at least, of the experimental points in figure 9 (B) have been affected by one or more variables other than the physical properties of the alloy and the form and relative size of the notch. This conclusion is based on a study of the positions of the experimental points in comparison with the physical properties recorded by Ludwik (14). One example of such comparison may be cited. A low-carbon steel with tensile

strength about 42,000 lb is represented in the figure by an exceptionally low point, whereas 3 other low-carbon steels with tensile strength ranging from about 40,000 to 55,000 lb are represented by points much higher in the diagram. And yet the steel represented by the low point differs little in tensile properties from the other three steels. Similar comparison for the other exceptionally low points in the figure reveals no reason for the very low apparent notch sensitivity of these steels. The positions of some experimental points, therefore, probably have been influenced by one or more undesired variables.

Local work-hardening during the formation of the notch may account for these low points. Such strengthening of the metal around the notch, in the region of highest stress concentration, would raise the fatigue limit of the specimen and thus diminish the apparent damage. The fact that susceptibility to work-hardening during notch formation is greater for soft than for hard steels, may account for the exceptionally low notch sensitivity obtained by Ludwik and Scheu with some of their soft steels. No exceptionally low sensitivity was obtained with their hard steels.

The region of high stress concentration around a notch decreases in size with increase in sharpness and decrease in absolute size of the notch. The thin layer of metal work-hardened during notch formation, therefore, may include only a small part of the region of high stress concentration around a large notch, but may include all the region of high stress concentration around a small notch. Work-hardening during notch formation, consequently, may have little effect on the damage due to a large notch, but may greatly reduce the apparent damage due to a small notch. The small notch used by Ludwik and Scheu evidently would be especially susceptible to the effects of work-hardening during notch formation.

For the reasons mentioned, therefore, the exceptionally low points in figure 9 (B) probably should be given little weight in estimating the probable form and position of the composite curve. The upper boundary of the area covered by the experimental points probably represents (in qualitative curvature, though not in position) the ideal composite curve. This boundary is similar in form to the curves in figures 3, 4, and 7. A composite curve, giving full weight to all the experimental points in figure 9 (B), however, would correspond rather closely to the 25-day corrosion curve. If the exceptionally low points be disregarded, the composite curve would correspond approximately with the 50-day corrosion curve. If effects of local work-hardening during notch formation could be entirely prevented, the curve probably would be higher. For comparison with results obtained by other investigators, however, the composite curve has been given the form and position of the 50-day corrosion curve.

With austenitic steels (a valve steel and a stainless steel) not represented in figure 9, the percentages of damage obtained by Ludwik were 6 and 0, respectively. These low results are in general agreement with results obtained by Houdremont and Mailander. The evidence apparently indicates that notches are less damaging to austenitic steels than to other steels. The apparently low notch sensitivity of austenitic steels may be due, in part at least, to their high work-hardening rate or capacity. During notch formation, work hardening would be greater for austenitic steels than for other steels. Consideration will be given later to the possible influence of local hardening during a fatigue test.

7. MISCELLANEOUS DATA ILLUSTRATING THE INFLUENCE OF TENSILE STRENGTH ON NOTCH SENSITIVITY OF STEELS

Further evidence as to the forms of the ideal composite curves for steels is given in figure 8. Nine of the 13 miscellaneous curves in this figure, drawn so as to give due weight to each experimental point, are similar in form to the curves for corroded specimens in figures 3 and 4. They also form a consistent series. The other 4 curves in figure 8, each based on only 2 experimental points, are drawn so that all 13 curves form a consistent series, which (with practically no change) would fit into the series of stressless corrosion curves at the right of figure 4.

The evidence presented in figures 7, 8, and 9, therefore, confirms the assumption that each stressless corrosion curve in figures 3 and 4, represents the effect of a notch of practically constant effective sharpness. The curves in all these figures, consequently, illustrate average relationship between notch sensitivity and tensile strength of ordinary steels. The series of curves at the right of figure 4, moreover, illustrates the change in position and form of the curve, with change in effective sharpness of notch.

8. RELATIVE EFFECT OF NOTCHES ON TORSIONAL AND FLEXURAL FATIGUE. INFLUENCE OF FILLETS, KEYWAYS, AND SURFACE ROUGHNESS

Although the graphs in figure 8 were assembled primarily as confirmatory evidence for the forms of the ideal composite curves for steels, these graphs also illustrate other relationships of theoretical and practical importance. Although space is not available for adequate discussion, mention will be made of a few of these relationships.

The theoretical ratio between stress concentration factors due to torsion and tension (or bending) varies with the form of the notch. For a circumferential groove, the ratio is $\dfrac{1+\sqrt{\dfrac{d}{r}}}{1+2\sqrt{\dfrac{d}{r}}}$.

For values of $\dfrac{d}{r}$ ranging from 1 to 9, this ratio ranges from ⅔ to ⅐. The corresponding ratio of percentage-decreases in the fatigue limit, however, ranges from 0.75 to about 0.84. Ratios of this order are obtained by comparison of corresponding ordinates for two pairs of curves (13, 14) in figure 8 (B). One of these pairs represents the influence of a sharp groove on torsional and flexural fatigue; the other pair represents the influence of a fillet. (Curve A has been reproduced from figure 9 (B).) The ordinate ratios for these 2 pairs are about 0.70 and 0.74, respectively. The evidence, therefore, confirms the theoretical conclusion that the effect of a circumferential groove or fillet is much less in torsional than in flexural fatigue.

For a transverse cylindrical hole in a cylindrical specimen, the theoretical ratio between torsional and flexural stress concentration factors is 4/3. Unlike a circumferential groove, therefore, such a hole should be slightly more damaging in torsional than in flexural fatigue. In agreement with theory, the torsional-fatigue curve 1 of figure 8 (A) is slightly higher in the diagram than the flexural-

fatigue curve in figure 9 (A) (which represents a $\frac{d}{r}$ ratio of 1.0), and is also slightly higher than the flexural fatigue curve of figure 8 (A), which represents the effect of a bored conical depression (1). The available evidence therefore, confirms the theoretical conclusion that a transverse cylindrical hole is slightly more damaging in torsional than in flexural fatigue.

A key way of the profile type, as illustrated in figure 8 (A) by 2 graphs representing results obtained by different investigators (5,29), apparently has much less effect in torsional than in flexural fatigue. In its relative effect on torsional and flexural fatigue, therefore, this longitudinal groove (in agreement with theory) evidently resembles more nearly a circumferential groove than a transverse cylindrical hole.

The influence of various methods of finishing the surface of a specimen is illustrated in figure 8 (A) by composite graphs (1, 23, 33). Space is not available for discussing this subject.

9. INFLUENCE OF A NOTCH ON THE FATIGUE LIMIT OF ALUMINUM ALLOYS; DATA OF LUDWIK AND SCHEU, AND OF R. R. MOORE

Ludwik and Scheu (12,13,14), using the same form of notch that they used for steels, investigated the effect of a notch on fatigue of aluminum alloys. R. R. Moore (26,27) also investigated the effect of a notch on aluminum alloys, using a groove 0.038 in. deep, with root raidus 0.01 in. The ratio $\frac{d}{r}$, therefore, was practically the same as for the notch used by Ludwik and Scheu. Results obtained in both investigations are included in figure 9 (C). For comparision, composite curves have been reproduced representing results obtained at Annapolis and results obtained by Ludwik and Scheu with steels.

Two experimental points in figure 9 (C) represent cold-worked alloys; the other experimental points represent alloys that were not in the cold-worked condition. As the influence of cold working and the influence of composition and heat-treatment on notch sensitivity probably should not be represented by the same composite curve, the 2 cold-worked alloys and the alloys that had not been cold-worked have been represented by 3 different curves, L, M, and N. Curve N representing severely cold-worked aluminum, is much steeper than curve L representing alloys not in the cold-worked condition. Curve M, representing an alloy that had been cold drawn after heat treatment, is only slightly steeper than curve L. These differences in slope between curves L, M, and N probably are due to differences in the degree of cold working received by the corresponding alloys. The evidence seems to indicate that increase in strength due to cold working causes greater increase in notch sensitivity than does the same increase in strength due to composition or heat treatment. Additional evidence on this subject will be presented later.

The scatter of results obtained by Ludwik and Scheu with aluminum alloys, as represented by graph L, is as great as the scatter obtained by the same investigators with steels. For reasons previously discussed, however, some of the experimental points probably are too ow. With annealed duralumin, for example, percentage damage

obtained was 33.3. With duralumin hardened by heat treatment, however, percentage damage was only 3.5. With another hardened alloy differing little in composition from duralumin, percentage damage was 40.0. The percentage damage obtained with hardened duralumin, therefore, probably is much too small. For these reasons, the composite curve representing alloys that were not in the cold-worked condition has been drawn with little regard for the three exceptionally low experimental points.

This curve is far above the curve for steel specimens with the same notch ratio, and is even slightly above the curve for steel specimens with much sharper notch. Notch sensitivity of aluminum alloys, therefore, seems to be as great as the sensitivity of much stronger steels. The relative steepness of slope of the stressless-corrosion curves for aluminum alloys in figures 3 and 4, consequently, appears to be due chiefly to relatively great notch sensitivity rather than to sharper corrosion pitting.

10. INFLUENCE OF A NOTCH ON THE FATIGUE LIMIT OF MAGNESIUM ALLOYS: DATA OF R. R. MOORE

Results obtained by R. R. Moore (25,26) with magnesium alloys, using the same form of notch that he used with aluminum alloys, are shown in figure 9 (D). In the same figure are reproduced composite curves representing results obtained by other investigators with steels.

A composite curve to represent the results obtained with magnesium alloys has been drawn from the origin of coordinates through the mean position of the experimental points: The curvature has been made to correspond with that of the curves for steels. The curve for magnesium alloys is far above the curve representing the effect of a notch of about the same shape on steels, and is even above the curve for steel specimens with a much sharper notch.

Notch sensitivity for magnesium alloys, therefore, probably is at least as great as for aluminum alloys, and is as great as the sensitivity of much stronger steels.

IV. NOTCH SENSITIVITY AND ITS RELATIONSHIP TO OTHER PROPERTIES OF METALS

1. NOTCH SENSITIVITY

Various quantitative indices of notch sensitivity have been proposed. Some of these are based on relationship between actual and theoretical damage. The theoretical stress concentration factor, however, is not readily estimated, because of the influence of relative and absolute size of notch. The percentage decrease in the fatigue limit, due to a notch, is used in this paper as an index of notch sensitivity. Relative notch sensitivities are indicated by the relative magnitudes of the ordinates in diagrams of the type shown in figures 3, 4, 7, 8, and 9. In any such comparison, however, consideration must be given to differences in sharpness of notch and kind of stress.

2. NOTCH TOUGHNESS

Notch toughness probably should not be considered as the opposite of notch sensitivity, but as a combination of 2 variables, notch sensitivity and strength. Of two metals with equal notch sensitivity, the

stronger metal should be considered the tougher. To decide whether a weak metal with low notch sensitivity is tougher or less tough than a strong metal with high notch sensitivity, however, may be difficult. Nevertheless, a generally useful index of notch toughness of a metal (as illustrated by a diagram of the type shown in fig. 9) is the angle between the vertical and a line drawn from the origin of coordinates to the corresponding experimental point. Notch toughness increases with this angle. In any such comparison of metals, however, consideration must be given to differences in sharpness of notch and kind of stress.

Comparison of all the metals represented in figures 7 and 9 indicates that notch toughness is considerably less for copper, aluminum alloys, and magnesium alloys than for ordinary steels. For ordinary nickel-copper alloys with nickel content ranging from that of commercial nickel down to 20 percent or possibly less, as shown in figure 7, notch toughness probably is no less than for ordinary steels. For corrosion-resistant steels, as indicated by the data of Houdremont and Mailander (10) and also by data obtained by Ludwick (14), notch toughness evidently is greater than for carbon steels and ordinary alloy steels.

3. RELATIONSHIP OF NOTCH SENSITIVITY TO DUCTILITY

Notch sensitivity tends to decrease with increase in ductility. This general relationship between notch sensitivity and ductility is sometimes attributed to a surmised influence of ductility in favoring local yielding and consequent relief of stress concentration. It does not seem probable, however, that the degree of relief of stress concentration would depend on the ductility as measured by total deformation at fracture. There are reasons for doubting, moreover, that notch sensitivity depends largely on ductility as such, though it may depend on another property that is roughly proportional to total tensile elongation.

4. RELATIONSHIP OF NOTCH SENSITIVITY TO MECHANICAL HYSTERESIS

Attempts have been made recently to correlate notch sensitivity with mechanical hysteresis. Extensive investigation of this subject has been made by O. Foppl and his coworkers at the Wohler Institute. (The terms "damping capacity", and "dynamic ductility", used by these investigators, have no apparent advantage over the older name, mechanical hysteresis.)

According to the views of Foppl and his associates (11), high hysteresis value is accompanied by low notch sensitivity and vice versa. Data presented in support of this idea, however, are not conclusive. Although examples that apparently support the idea have been pointed out, there are also many discrepancies. For one such example, mention may be made of annealed copper. Although notch sensitivity of this metal is high, hysteresis also is high.

Hysteresis depends not only on the composition of the metal, on the mechanical and thermal treatment, and on the applied stress range, but also on the previously applied cycles of stress. The variation of hysteresis with stress range and with repetition of stress, has been studied by a number of investigators (2,4,6,8,11,15,16).

With repetition of cycles at constant stress range, hysteresis may increase at a decreasing rate, so as to approach a maximum; or it may decrease at a decreasing rate from the initial value (which may be large) to a minimum. For some metals, this minimum may possibly be an equilibrium value, which will prevail for an indefinitely large number of cycles. According to published results of experiments continued for many cycles, however, hysteresis sometimes may increase again at a decreasing rate. Both the decrease in hysteresis and the decrease in the rate of increase, are due to hardening of the metal under cyclic deformation. Moreover, the rate of hardening caused by cyclic deformation, like the rate of hardening caused by continuous deformation in one direction, continually decreases.

Increase of hysteresis at a decreasing rate, may occur whether or not the stress is above the fatigue limit. If the stress is above the fatigue limit, hysteresis eventually begins to increase at an increasing rate, and thus continues until the specimen fails. If the stress is below the fatigue limit, however, hysteresis eventually reaches a maximum and thereafter may slowly decrease. Such final decrease from a maximum probably is not uncommon. Haigh (8) has observed instances of increase during several million cycles, followed by slow decrease during about 30,000,000 cycles. Ludwik (14) has published curves illustrating the changes in hysteresis with cyclic stress at the fatigue limit. As indicated by a series of curves representing a great variety of annealed carbon steels, hysteresis first increased to a maximum and then gradually decreased. The number of cycles required to reach the maximum varied more than a hundredfold, with the carbon content of the steel. The gradual decrease from the maximum continued far beyond 10,000,000 cycles, and in some instances an equilibrium value had not been reached after a hundred million cycles.

Eventually, under cyclic stress at or below the fatigue limit, hysteresis reaches a value that thereafter remains constant. This condition is known as "elastic hysteresis." As shown by several investigators (9, 32), elastic hysteresis is appreciable even under very minute stress. As the relationship between initial hysteresis and elastic hysteresis (at the fatigue limit) differs greatly for different metals, comparison of initial hysteresis values for various metals, gives no means of comparison of elastic hysteresis values.

In a notched specimen, hysteresis causes the stress concentration to be less than the theoretical value. This effect of hysteresis, therefore, causes the fatigue limit of a notched specimen to be relatively high, and thus decreases the notch sensitivity. Elevation of the fatigue limit due to the stress-lowering effect of hysteresis, however, probably depends less on the initial hysteresis than on the elastic hysteresis at the fatigue limit. Initial hysteresis, as it gives no information about elastic hysteresis, cannot be used as a measure of notch sensitivity.

5. RELATIONSHIP OF NOTCH SENSITIVITY TO WORK-HARDENING DUE TO CYCLIC STRESS

Although stress lowering due to elastic hysteresis doubtless has some effect on notch sensitivity, another influence of cyclic stress may have greater effect. The effect of a notch on the fatigue limit may depend not only on the stress concentration, but also on the amount

of local work-hardening accompanying the progress from initial to elastic hysteresis.

Although all metals are more or less work-hardened by cyclic stress at the fatigue limit, the strengthening influence is most conspicuous for fully annealed metals and single-phase alloys. For such materials, the fatigue limit is far above the initial elastic limit, and is even above the initial tensile proof stress. (By "proof stress" is meant the stress that, after release of load, will result in permanent elongation of 0.0001 in. per inch length). During the progress from initially large hysteresis to elastic hysteresis, the metal in the most highly stressed parts of the specimen is work-hardened, and the elastic range is increased until it practically coincides with the fatigue range (within the limitations of elastic hysteresis).

The amount and distribution of the work-hardening during the progress from initial to elastic hysteresis, however, depend not only on the fundamental properties of the metal and on the nominal cyclic stress, but also on the specific conditions that determine the constancy or variation of the actual stress and strain throughout the test. For this reason, the fatigue limit is not a fundamental property of the metal, but depends somewhat on the impressed conditions of the test. By gradual increase of stress from below the ordinary fatigue limit, the limit may be raised. Even by cyclic stress above the fatigue limit (as indicated by unpublished results of experiments by one of the authors), it appears possible that the fatigue limit may be raised, provided the number of cycles of overstress is less than a critical value, which depends on the metal and on the overstress. The specific conditions in a fatigue test often are such that the actual stress increases while the nominal stress remains constant. In a rotating-beam specimen, for example, the progress from initial to elastic hysteresis is accompanied by a change in stress distribution. As the final change in hysteresis (when the nominal stress is just below the fatigue limit) probably always is a decrease, the stress distribution from axis to circumference becomes more nearly linear, and the stress at the circumference thus approaches the fatigue limit from below. For this reason, the fatigue limit obtained by rotating-beam test theoretically would be higher than that obtained by direct tension-compression test. The idea that the fatigue limit is appreciably influenced by the specific conditions of the test, moreover, is supported by evidence based on experiments of a number of investigators.

The stress gradient in a rotating-beam specimen makes possible a gradual rise of actual stress to the fatigue limit. A more pronounced rise to the fatigue limit probably results from the steeper stress gradient around a notch. Local elevation of the fatigue limit due to rising cyclic stress, therefore, tends to be greater in a notched than in an unnotched specimen. The greater this local elevation of the fatigue limit, the steeper is the hardness gradient opposing the influence of the stress gradient and thus decreasing the apparent notch sensitivity.

6. TENSILE WORK-HARDENING CAPACITY

The steepness of the hardness gradient around a notch possibly depends on the work-hardening capacity of the metal. According to this view, therefore, notch sensitivity depends considerably on

work-hardening capacity. The rate of increase of hardness with cold work would influence the amount of work-hardening per cycle, and thus would determine the number of cycles necessary for hardness to reach its maximum. Though maximum hardness may depend somewhat on the amount of work-hardening per cycle, however, it probably depends much more on work-hardening capacity. Notch sensitivity, therefore, probably depends less on rate of work-hardening than on work-hardening capacity.

To determine whether there is experimental evidence of significant relationship between work-hardening capacity and notch sensitivity, it is necessary to compare corresponding values of these two properties for a great variety of metals and alloys. Some evidence on this subject is available, based on notch effects of stressless corrosion and on the corresponding "tensile work-hardening capacities." These data, obtained by one of the authors while employed at the U.S. Naval Engineering Experiment Station, have recently been compared and correlated. The results of the correlation are presented in table 3 and in figures 10 and 11.

Tensile work-hardening capacity may be estimated by comparing some other tensile property with the maximum stress obtainable in tension, the true breaking stress (actual breaking load divided by the sectional area at fracture). For comparison with the true breaking stress, the proof stress was tried, but the relationship proved too erratic. Tensile strength finally was chosen for this purpose. After trial of various indices based on the relationships between the two properties, the index finally chosen was the percentage ratio of tensile strength to true breaking stress; this ratio will be called the "percentage strength." Maximum hardness obtainable by pure tensile stress (hardness independent of cold working previous to the tension test) is thus considered as 100 percent. Percentage strength subtracted from 100 evidently may be used as a direct index of work-hardening capacity.

7. RELATIONSHIP BETWEEN PERCENTAGE STRENGTH, WORK-HARDENING CAPACITY, AND TENSILE STRENGTH

Relationship between percentage strength and tensile strength, for a great variety of metals and alloys, is illustrated in figures 10 and 11. Ordinates measured from the bottom of the figure represent percentage strength; ordinates measured from the top represent work-hardening capacity.

The straight broken lines in figures 10 and 11 represent the influence of cold work on the relationship between tensile strength and work-hardening capacity. The intersection of each of these lines with the line representing zero work-hardening capacity is at an abscissa representing the true breaking stress; each of these intersections represents a metal or alloy that has been cold-worked (by tension) until the tensile strength equals the true breaking stress. Because of the relationship between ordinate and abscissa in a diagram of this type, the lines point toward the origin of coordinates. In figure 10, the graphs represent results of tension tests on metals that (at the beginning of the test) were not work-hardened. In figure 11, the graphs represent results of tests of both annealed and cold-worked metals.

The broken lines in figure 11, with two exceptions, represent nonferrous metals. The two exceptions are lines representing results obtained by O'Neill (28) with two samples of steel wire. These wires were cold-drawn to various degrees of hardness and an ordinary tension test was made at each stage. The true breaking stress, as O'Neill expected, was practically independent of the amount of previous cold drawing. The straight lines in figure 11 are drawn to the average values of the true breaking stress.

The lowest plotted symbol, for each of the metals represented in figure 11, is based on the result of a tension test of fully annealed metal; each higher plotted symbol represents the result of a tension test of metal that had been previously cold-worked.

The true breaking stress obtained with cold-worked metal, as shown in table 3, is sometimes higher and sometimes lower than that obtained with fully annealed metal. The differences, though sometimes rather large, are no greater than would be expected in view of the difficulty of obtaining an accurate value for this property.

As the metals represented in figure 10 had not been work-hardened, differences in physical properties depend on differences in composition and heat treatment. The steels represented in this figure include those represented in figure 3, in the graph showing the effect of 10 days' stressless corrosion. They also include additional steels, most of which were tested at the U.S. Naval Experiment Station; properties of a few of the steels of highest strength were obtained from data published by Gillett and Mack (3). The composite curve drawn to represent the relation between percentage strength and tensile strength for carbon steels and ordinary alloy steels, is similar in form to curves representing the relation between tensile strength and notch sensitivity. Best comparison can be made with the curve in figure 3 representing the notch effect of 10 days' stressless corrosion. To facilitate comparison of corresponding experimental points in the 2 figures, each steel represented in figure 3 has been given an identification number, and the same numbers have been placed beside corresponding symbols in figure 10. These numbers are also listed in the first column of tables 2 and 3.

Prior to comparison of these 2 graphs, it had been assumed that the scatter of individual points in figure 3 is due chiefly to the unavoidable variations in intensity of corrosive attack, and to the natural scatter of points representing differences between the fatigue limits of corroded and uncorroded specimens. Comparison of the relative positions of the corresponding experimental points in the 2 graphs, however, apparently reveals some relationship between variations in notch sensitivity and variations in work-hardening capacity. The most striking relationship is between points 2, 3, 7, and 8 of the 2 figures. Each pair connected by a broken line represents the same sample of steel after 2 different heat treatments. Points 2 and 7 represent fully annealed steels; points 3 and 8 represent the same steels quenched and tempered. The position of these 2 pairs of points with reference to the composite curve in each figure is about the same. That this relationship is not due to chance appears probable, moreover, when comparison is made between the other corresponding points in the 2 figures. The distribution of 16 of the 24 points, above and below the composite curve in each figure, is qualitatively the same. Of the remaining 8 points, 2 are practically on the composite curve

in one of the figures. The fact that at least two-thirds of the points are similarly distributed with reference to the composite curve seems to indicate that the form of the composite curve and the variations in position of the experimental points depend somewhat on work-hardening capacity.

As indicated by the position of the 2 symbols representing corrosion-resistant steels, the percentage strength of these austenitic steels is considerably less than that of ordinary steels. The relatively low percentage strength (high work-hardening capacity) of these steels evidently corresponds qualitatively to their lower notch sensitivity.

Although the symbols representing aluminum alloys are widely scattered, a composite curve has been drawn to represent the average relationship between percentage strength and tensile strength. This curve is considerably above the curve representing steels. The relative positions of these 2 curves evidently are in accordance with the lower notch-toughness of aluminum alloys, illustrated in figure 9.

Figure 12 illustrates the relationship between tensile strength and the percentage elongation at fracture (in 2-inch gage length). The metals represented here are the same that are represented in figure 10. To facilitate comparison between figures 3, 10, and 12, identification numbers have been given to corresponding symbols. The curves in figure 12, if inverted, evidently would be similar to the corresponding curves in figure 10. This similarity, however, merely illustrates the fact that tensile elongation is a rough index of work-hardening capacity. It does not decide the question whether notch sensitivity is dependent chiefly on ductility as such, or on work-hardening capacity. Some evidence relative to this question, however, is obtained by comparing the distribution of individual results in figures 3, 10, and 12. The relative positions of symbols 2, 3, 7, and 8, which have been shown to be in good agreement in figures 3 and 10, are in poor agreement in figures 12 and 3. Less than half the numbered symbols in figure 12, moreover, are distributed conformably to those in figure 3, with reference to the composite curve. Comparison of figure 12 with figures 3 and 10, therefore, leads to the conclusion that notch sensitivity probably is more nearly related to percentage strength than to total elongation.

Relationship between elongation at maximum load (point of necking) and tensile strength, for the same metals and alloys, has been studied by means of a diagram not here shown. The curves in this diagram are similar in form to the curves in figure 12. The distribution of individual results, however, is little better than the distribution in figure 12. Notch sensitivity, therefore, appears to be more nearly related to percentage strength than to elongation at maximum load.

Because the straight broken lines in figure 11 converge toward the origin of coordinates, their slopes must decrease with increase in the true breaking stress. With the slopes of these straight lines may be compared the varying slope of the composite curve for steels, which has been reproduced in figure 11 as curve A. This curve, representing the influence of composition and heat treatment, differs greatly in slope and form from the lines representing the influence of cold working. The straight lines, at their intersections with curve A, are much steeper than this curve. The rate of decrease in work-hardening capacity with increase in strength, therefore (as might be

expected), is much greater when due to cold working than when due to composition or heat treatment.

If notch sensitivity depends largely on work-hardening capacity, increase in strength due to cold working evidently would cause greater increase in notch sensitivity than would the same increase in strength due to composition or heat treatment. This means that curves of the type shown in figures 3, 4, 7, and 9 would be steeper when they represent the influence of cold working than when they represent the influence of composition or heat treatment. Experimental evidence on this subject, though meager, seems to support the hypothesis. The curve for cold-worked aluminum in figure 9 (C), for example, is much steeper than the curve for aluminum alloys not cold worked. The curve for an aluminum alloy that had been cold drawn after heat treatment, moreover, is above the curve representing alloys that had not been cold worked. Although a separate curve for extruded magnesium has not been drawn in figure 9 (D), it is possible that this metal had received more cold work than the extruded or forged magnesium alloys. If this surmise is correct, the relatively high position of the point representing extruded magnesium is due to decreased work-hardening capacity caused by cold working. A few results obtained by Haigh and Beale (7) with cold-rolled strip steel, when compared with the curve in figure 7 representing steels that had not been cold worked, constitute additional evidence pointing in the same direction.

The relative positions of the composite curve for steels, the lines for aluminum alloys, and the point representing magnesium alloys are about the same in figures 10 and 11 as in figures 4 and 9. The relative position of the line for copper, moreover, is about the same in figure 11 as in figure 7. The available evidence seems to indicate that the general distribution of experimental points and lines for various metals and alloys in a percentage-strength diagram is qualitatively similar to the distribution of corresponding points and lines in a notch-sensitivity diagram. The only apparent discrepancies are in the positions of individual points representing fully annealed metals.

The high notch sensitivity of cold-worked copper is in accordance with the high percentage strength, as illustrated in figures 7 and 11, respectively. For fully annealed copper, however, notch sensitivity is too high to be in accordance with the percentage strength. For the other fully annealed metals and single-phase alloys represented in figure 11, moreover, percentage strength is not high; for some of these, in spite of their relatively high tensile strength, percentage strength is lower than for copper. And yet notch sensitivity of these metals, according to the meager evidence available, is not low. As shown in figure 7, for example, notch sensitivity is not much less for annealed nickel-copper alloys than for steels of the same strength. All these apparent exceptions to the general rule that notch sensitivity is closely related to percentage strength are metals whose fatigue limits are above (sometimes far above) their elastic limits. For annealed copper the fatigue limit is more than twice the tensile proof stress. Even for copper specimens with a sharp notch, as shown in a paper by one of the authors (21), the fatigue limit is higher than anything that could be called an elastic limit.

The fatigue limit of a fully annealed single-phase metal is essentially the fatigue limit of metal that has been considerably work-hardened.

In the most highly stressed part of a notched or unnotched specimen of such metal, after repeated stress at the fatigue limit, there is a layer of work-hardened metal. The hardened layer around a notch probably is much thicker in an annealed single-phase metal than in a metal whose fatigue limit does not greatly exceed the elastic limit. The work-hardening capacity of the metal in this layer is not the work-hardening capacity of fully annealed metal but has been considerably reduced by the cyclic deformation. (The rapidity of loss of work-hardening capacity with plastic deformation is illustrated by the fact that copper loses the greater part of its work-hardening capacity when the sectional area is reduced only 25 percent.) A notch in a fully annealed single-phase metal after repeated stress at the fatigue limit, therefore, is essentially a notch in metal that has been somewhat work-hardened. Notch sensitivity of a metal whose fatigue limit is far above the elastic limit, consequently, should not be compared with work-hardening capacity of fully annealed metal, but with work-hardening capacity of metal that has been somewhat cold-worked. The degree of cold-working suitable for such comparison, although it cannot be stated exactly, should be at least enough to raise the elastic range to equality with the endurance range (range of stress at the endurance limit).

Fully annealed metals and single-phase alloys, therefore, are not believed to be real exceptions to the rule that notch sensitivity is closely related to percentage strength. The available evidence seems to indicate that notch sensitivity of metals, while it is influenced by elastic hysteresis, depends largely on tensile work-hardening capacity. Further investigation of this subject, however, is needed.

V. INFLUENCE OF TENSILE STRENGTH ON THE FATIGUE LIMIT OF A NOTCHED SPECIMEN

1. THE TWO OPPOSING VARIABLES

It has been shown that percentage decrease in fatigue limit, due to a notch, increases with the tensile strength. The endurance limit of the metal (fatigue limit obtained with smooth specimens), however, also increases with the tensile strength. The nominal fatigue limit of a notched specimen, therefore, is influenced by 2 opposing variables, each increasing with the tensile strength. The resultant of these 2 variables determines how much of the advantage due to superior strength is offset by disadvantage due to higher notch sensitivity.

2. INFLUENCE OF TENSILE STRENGTH ON THE FATIGUE LIMIT OF NOTCHED SPECIMENS OF STEEL (NOT COLD-WORKED)

The variation of endurance limit with tensile strength has received consideration by a number of investigators. A composite curve for steels, based on a large amount of data assembled from various sources was published by Gillett and Mack on page 147 of their book (3). This curve has been reproduced in figure 13. For steels with tensile strength less than about 200,000 lb/in.^{2}, as indicated by the curve, the endurance limit is approximately proportional to the tensile strength. With increase in tensile strength above 200,000 lb, the ratio of endurance limit to tensile strength (endurance ratio) de-

creases. As this decrease probably is due in part to increasing internal stress, special treatment aimed at reduction of internal stress probably would raise the endurance ratio, for many of these hard steels, above the values represented by the uppermost curve. Nevertheless, this curve probably gives a correct indication of the results obtainable in present commercial practice.

By making use of this curve and any of the percentage-damage curves, in figures 3, 4, 7, 8, and 9, other curves may be constructed to represent the influence of tensile strength on the fatigue limit. Three such curves have been drawn in figure 13.

The curve representing 2 days' corrosion illustrates the influence of a shallow notch. With this notch, the advantage of superior tensile strength evidently is diminished slightly. The effect of a sharper notch is illustrated by the curve representing 10 days' corrosion. With this notch, much of the advantage of superior strength is lost, especially for a range of tensile strength above about 200,000 lb; for ranges of lower strength, considerable advantage of superior strength still remains. The effect of a still sharper notch is illustrated by the curve (derived from a curve in fig. 7) representing the influence of a notch with $\frac{d}{r}$ ratio 28.4. This notch eliminates practically all advantage of increase in tensile strength above about 100,000 lb; for ranges of lower strength, some advantage of superior strength still remains. With a much sharper notch, such as a crack or sharp internal flaw, all advantage of superior strength probably would disappear.

The lowest curve of figure 13, as drawn, slopes downward with increase of tensile strength above about 200,000 lb. Such downward slope appears possible on account of the decrease in endurance ratio with increasing tensile strength, as indicated by the curvature of the uppermost curve. If the endurance ratio did not so decrease, the fatigue limit of even a sharply notched specimen probably would not decrease with increasing tensile strength. Such decrease in fatigue limit, if it exists, probably is slight.

3. INFLUENCE OF WORK-HARDENING ON THE FATIGUE LIMIT OF A NOTCHED SPECIMEN

For some metals, such as copper and nickel-copper alloys (18,19,20), work-hardening increases the endurance limit about in proportion to the increase in tensile strength, provided the work-hardening does not exceed a certain degree, which varies with the metal. Beyond this degree, the endurance ratio decreases. For other alloys, such as copper-tin and copper-zinc alloys (18,19,20), the endurance ratio decreases with even moderate cold working.

The influence of work-hardening on the fatigue limit of a notched specimen evidently would depend on the influence of work-hardening on the endurance ratio. If the endurance ratio is approximately constant throughout a considerable range of work-hardening, the curves of variation of the fatigue limit with tensile strength would be similar in form to the curves for notched specimens in figure 13, with the exception of the descending portion at the right of the lowest curve. With increasing sharpness of notch, the curves (as they extend to the right) would approach a horizontal direction, but would not

descend. Superior strength would lose more or less of its advantage but would not be a disadvantage.

If the endurance ratio decreases with work-hardening, the loss of advantage of superior strength (caused by a notch) is greater than if the endurance ratio remains constant. The fatigue limit of a sharply notched specimen may even be less for severely cold-worked than for fully annealed material.

Moderately cold-worked metals with a notch of the form shown in figure 7, however, were found by one of the authors (21) to have about the same fatigue limit as the corresponding fully annealed metals.

4. INFLUENCE OF HEAT TREATMENT ON THE FATIGUE LIMIT OF NOTCHED SPECIMENS OF NONFERROUS ALLOYS

For some nonferrous alloys, increase of the endurance limit by heat-treatment is less than proportional to the increase in tensile strength. The loss of advantage of superior strength due to a notch, therefore, probably is greater for these alloys than for steels, with the possible exception of very hard steels. The fatigue limit of a sharply notched specimen may possibly be lower when such a nonferrous alloy is heat treated than when it is fully annealed. In use of such alloys, therefore, it is especially important to avoid sharp notches and other abrupt changes of section.

5. INFLUENCE OF INTERNAL FLAWS

Internal flaws lower the apparent notch sensitivity, as the effect of such flaws on the fatigue limit is relatively greater for smooth than for notched specimens. The foregoing discussion of the influence of notches, therefore, is based on the assumption that the metal does not contain internal flaws of size comparable with that of the notch. It does not apply to a metal such as cast iron, of which the continuity is broken by particles of graphite.

The ratio between endurance limit and tensile strength of smooth specimens is greatly influenced by internal flaws. Such flaws in metal hardened by either heat treatment or cold work cause the endurance ratio to be less for hardened than for annealed metal. A line representing smooth specimens of metal with internal flaws, therefore, would be more or less curved like the lines in figure 13 representing outwardly notched specimens. Internal flaws thus may be the chief cause of the curvilinear relationship between endurance limit and tensile strength of some commercial alloys. An external notch in such metal evidently would remove less of the advantage of superior strength than if the curvilinear relationship were due to inherent properties of the metal.

A general résumé of technical information on spring materials is being prepared by cooperation of American Steel Foundries and the National Bureau of Standards, for eventual publication by the special research committee on mechanical springs, American Society of Mechanical Engineers. The present paper considers one phase of the subject. This paper was presented orally (by Dr. H. J. Gough of the National Physical Laboratory) at the Fourth International Congress for Applied Mechanics, Cambridge, England, July 9, 1934, and was published in abstract form by the Congress under the title "Relationship Between Notch Sensitivity and Other Properties of Metals."

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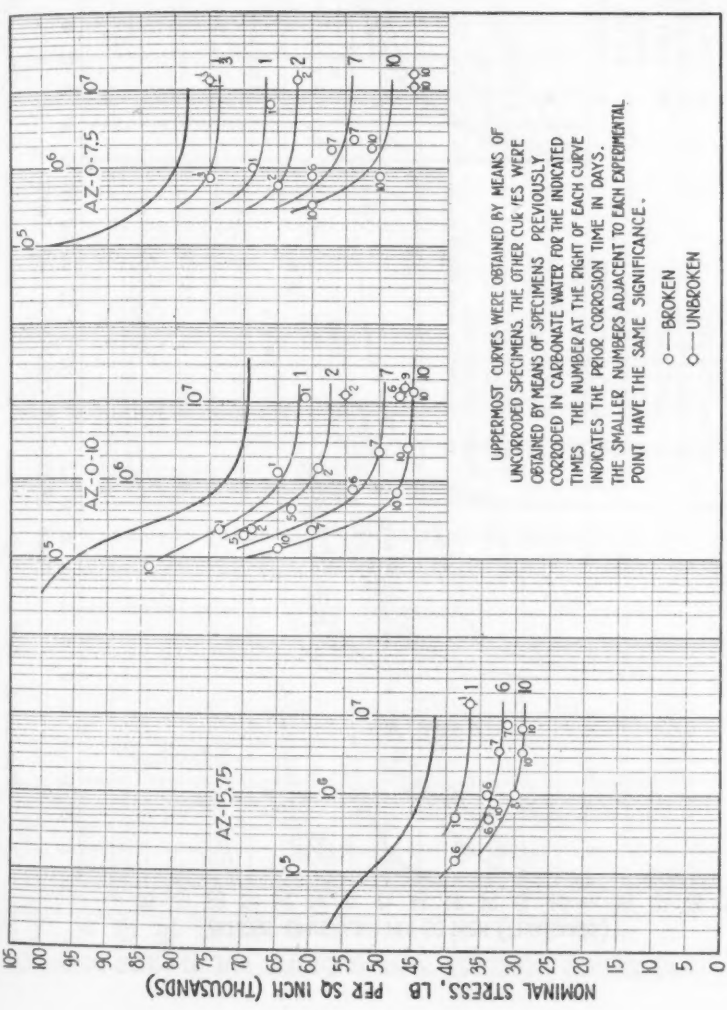
AZ-0-7.5
AZ-0-10
AZ-15.75
UPPERMOST CURVES WERE OBTAINED BY MEANS OF UNCORRODED SPECIMENS. THE OTHER CURVES WERE OBTAINED BY MEANS OF SPECIMENS PREVIOUSLY CORRODED IN CARBONATE WATER FOR THE INDICATED TIMES. THE NUMBER AT THE RIGHT OF EACH CURVE INDICATES THE PRIOR CORROSION TIME IN DAYS. THE SMALLER NUMBERS ADJACENT TO EACH EXPERIMENTAL POINT HAVE THE SAME SIGNIFICANCE.
○—BROKEN
◇—UNBROKEN
NUMBER OF CYCLES, LOGARITHMIC SCALE
NOMINAL STRESS, LB PER SQ INCH (THOUSANDS)

FIGURE 1.—*Influence of prior stressless corrosion of steels on the position of the stress-cycle graph.*

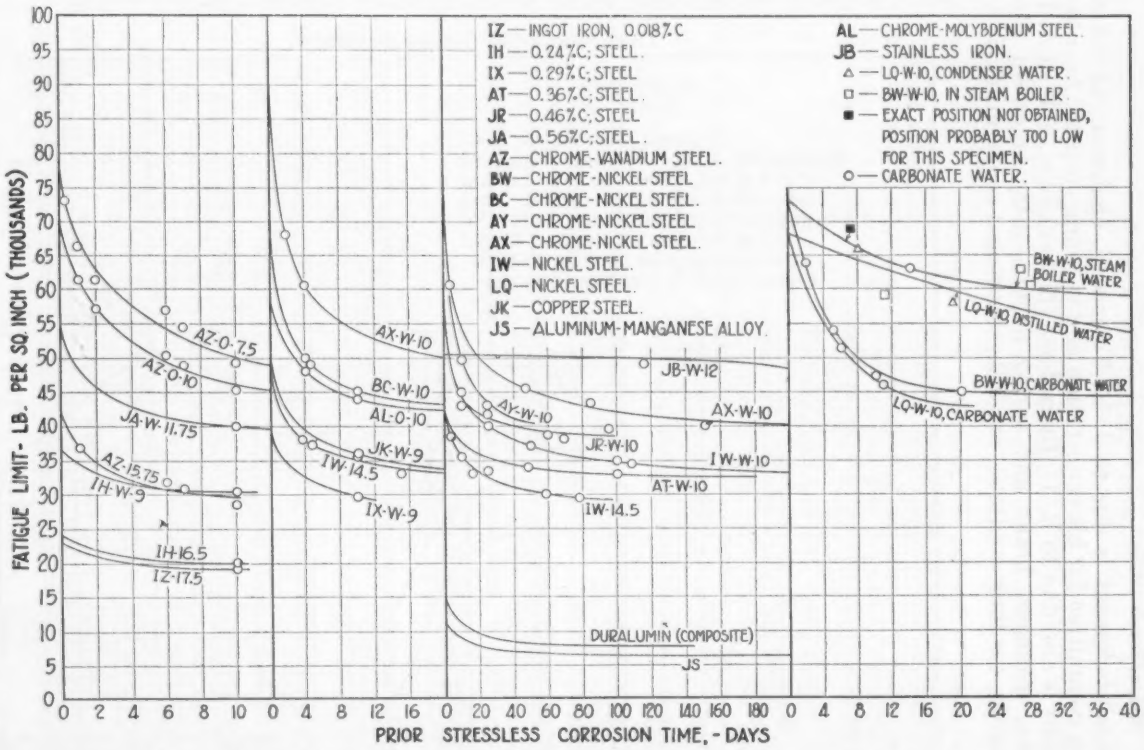

FIGURE 2.—*Influence of duration of prior stressless corrosion on the fatigue limit.*

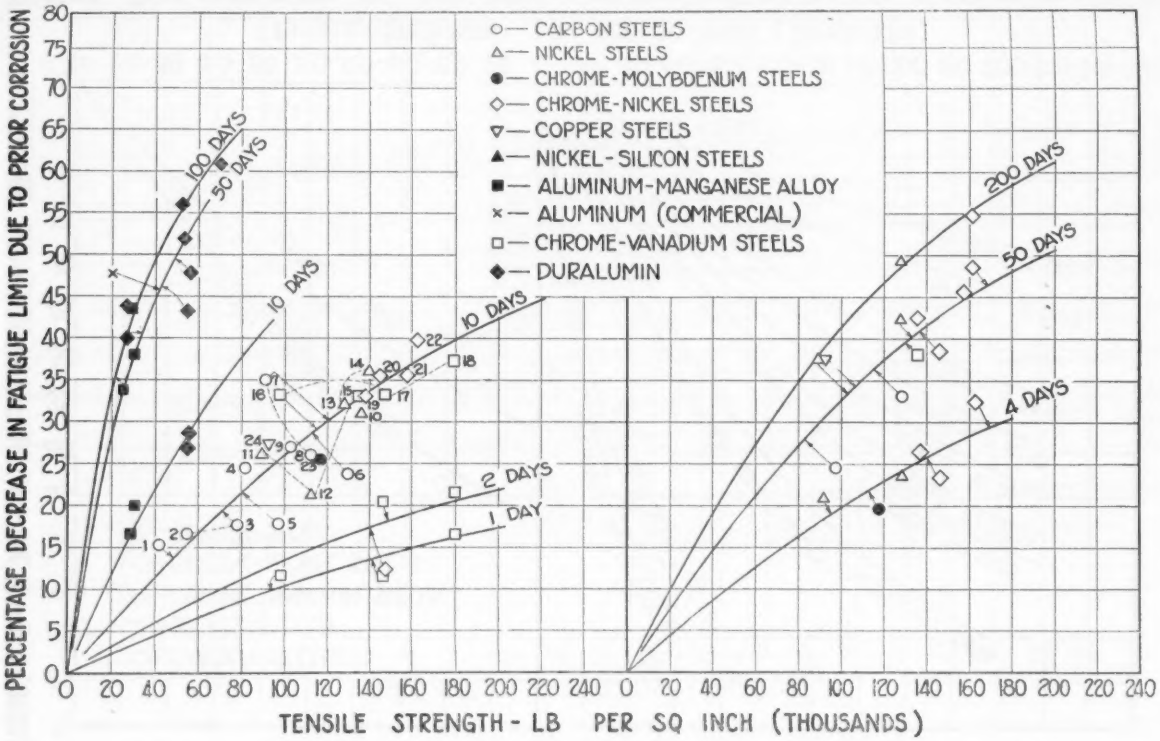

FIGURE 3.—*Relation between tensile strength and percentage decrease in fatigue limit of steels due to stressless corrosion.*

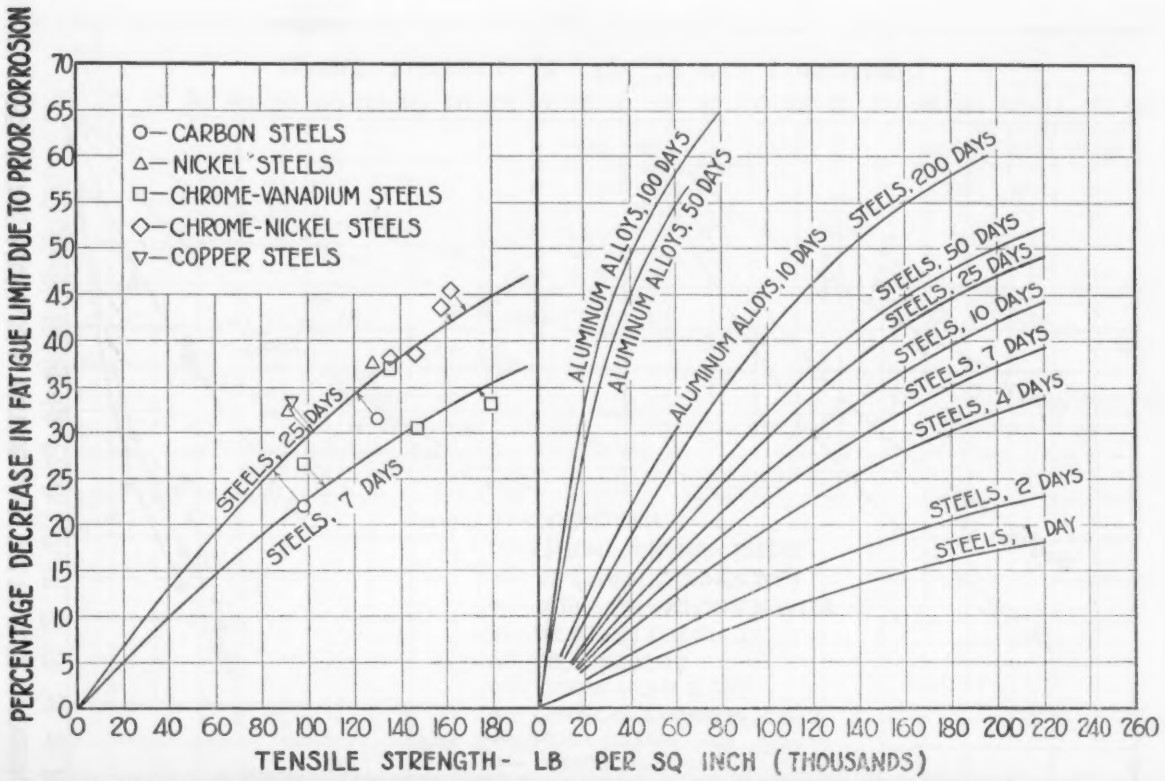

FIGURE 4.—*Relation between tensile strength and the percentage decrease in fatigue limit of steels due to stressless corrosion.*

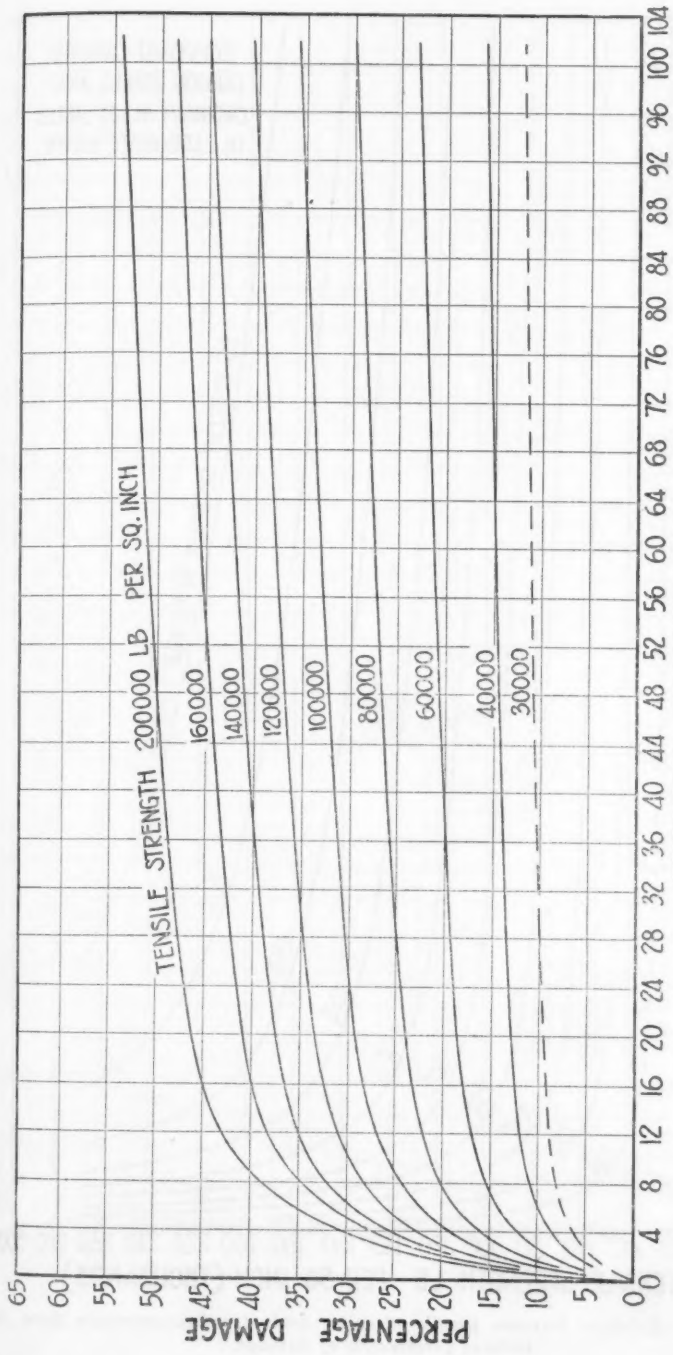

FIGURE 5.—*Relation between stressless-corrosion time and the percentage decrease in fatigue limit of carbon steels and ordinary alloy steels.*

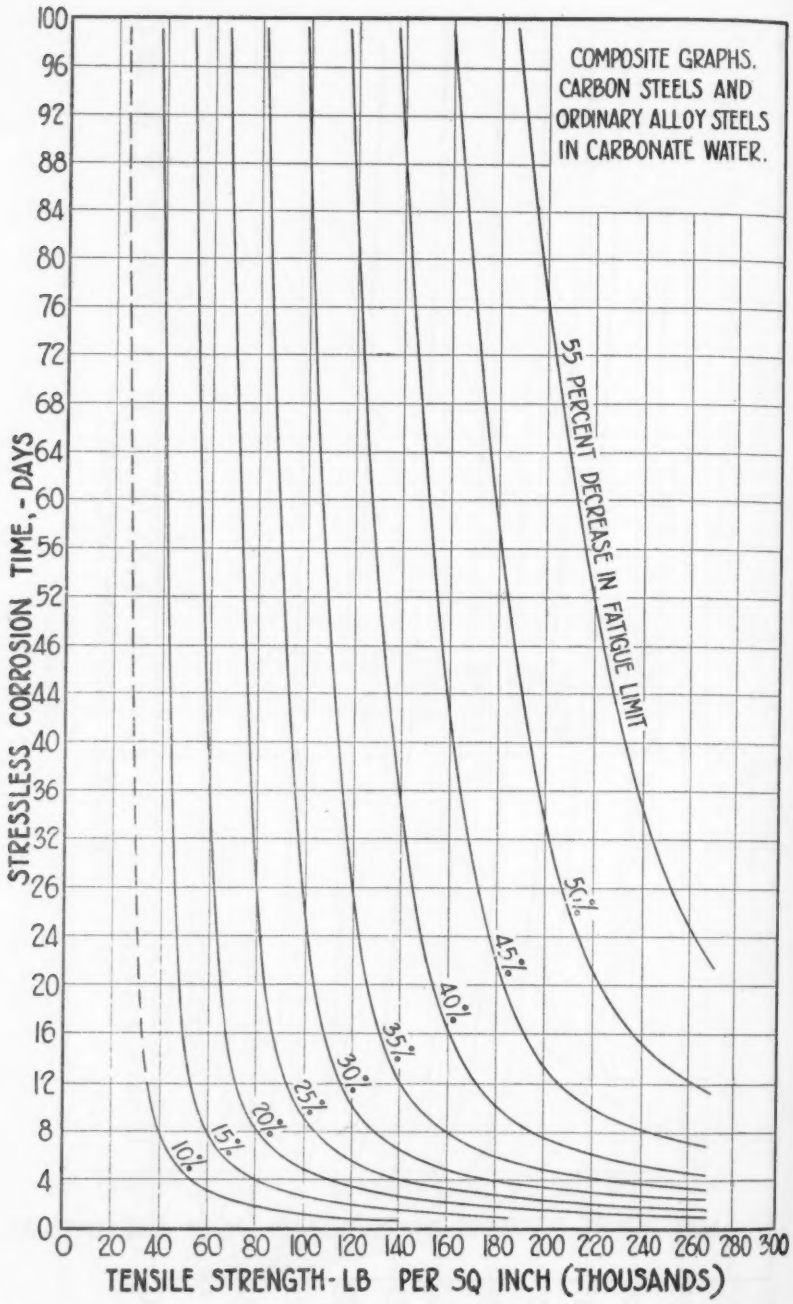
COMPOSITE GRAPHS.
CARBON STEELS AND
ORDINARY ALLOY STEELS
IN CARBONATE WATER.
55 PERCENT DECREASE IN FATIGUE LIMIT
50%
45%
40%
35%
30%
25%
20%
15%
10%
STRESSLESS CORROSION TIME, - DAYS
0 4 8 12 16 20 24 26 32 36 40 44 46 52 56 60 64 68 72 76 80 84 88 92 96 100
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
TENSILE STRENGTH - LB PER SQ INCH (THOUSANDS)

FIGURE 6.—*Relation between tensile strength and stressless-corrosion time, for various percentages of damage.*

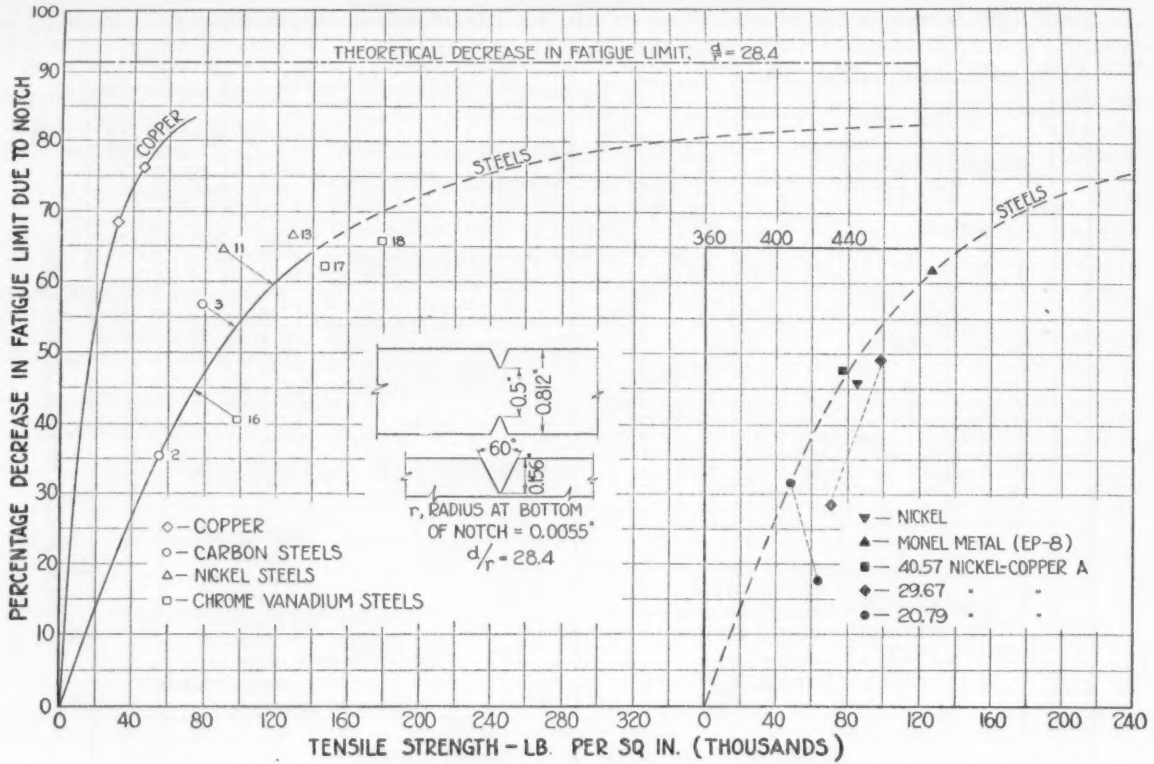

FIGURE 7.—*Relation between tensile strength and the percentage decrease in fatigue limit due to a mechanically formed notch.*

93280—34—9

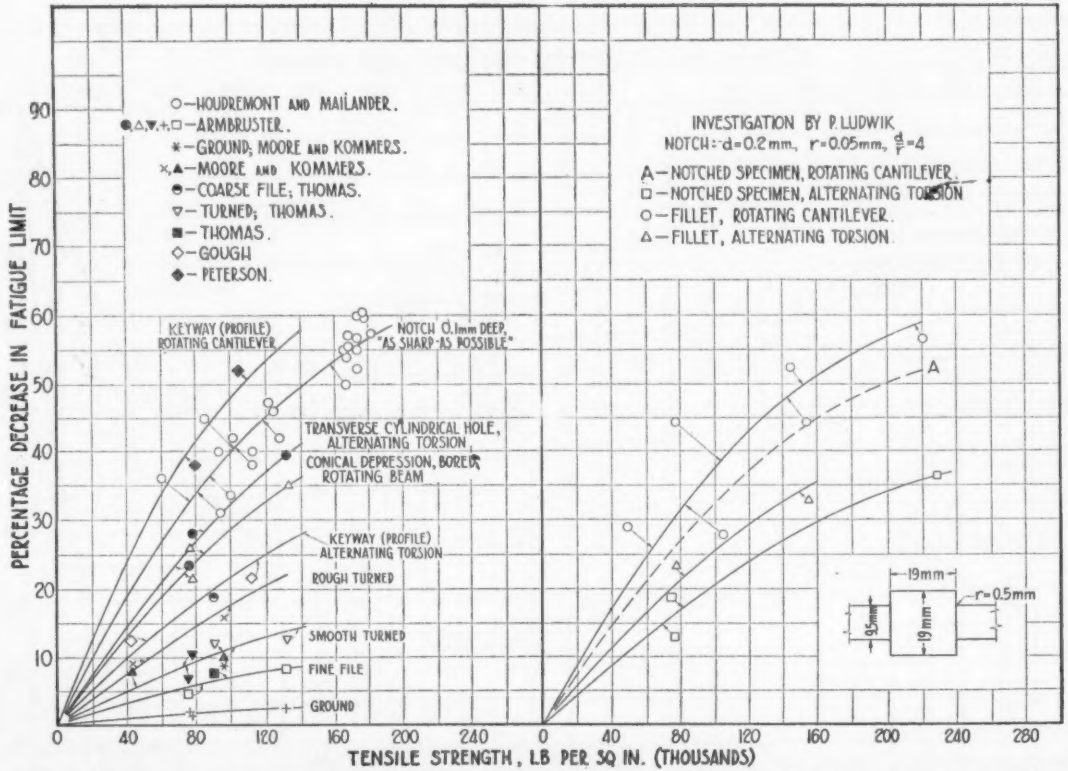

FIGURE 8.—*Relation between tensile strength and the percentage damage due to grooves, holes, fillets, keyways, depressions, and surface roughness.*

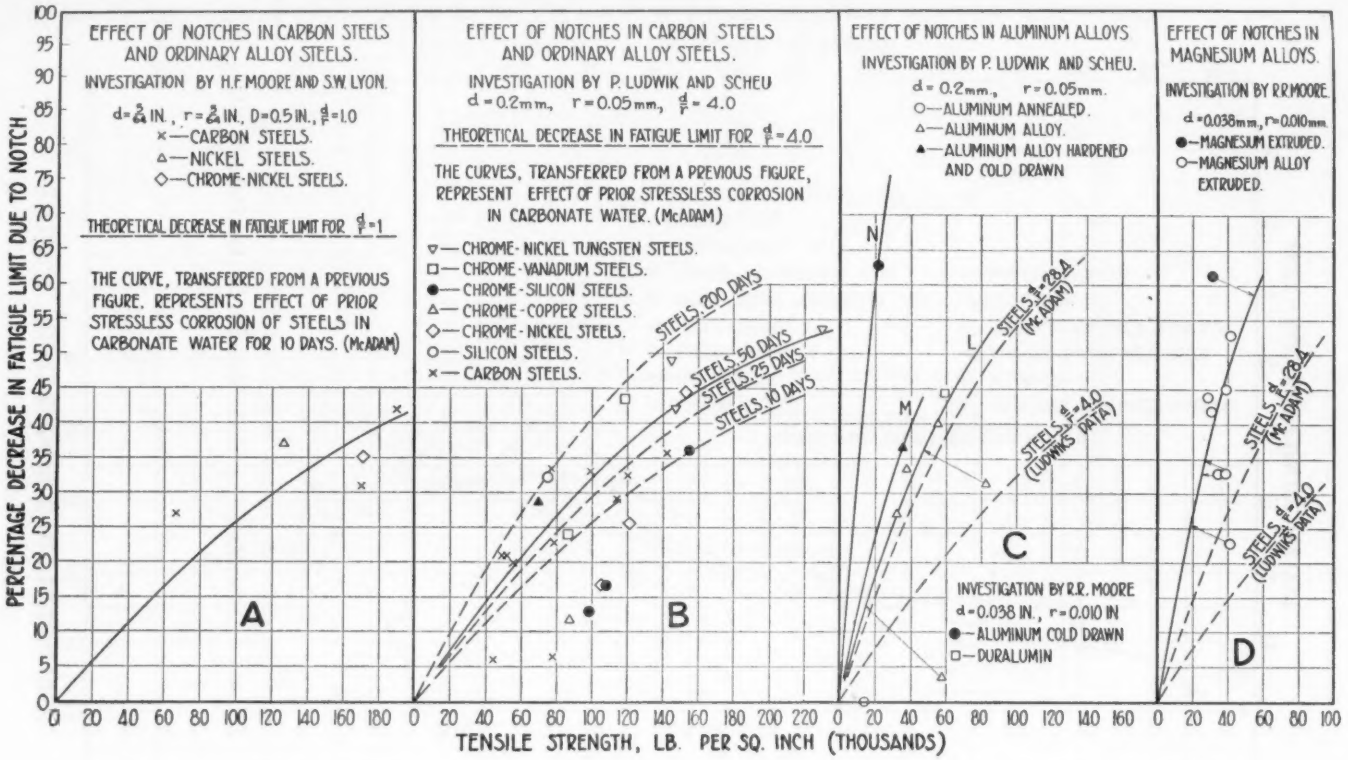
EFFECT OF NOTCHES IN CARBON STEELS AND ORDINARY ALLOY STEELS.
INVESTIGATION BY H.F MOORE AND S.W. LYON.
d=⅝ IN., r=⅛ IN., D=0.5 IN., d/r=1.0
×—CARBON STEELS.
△—NICKEL STEELS.
◇—CHROME-NICKEL STEELS.
THEORETICAL DECREASE IN FATIGUE LIMIT FOR d/r=1
THE CURVE, TRANSFERRED FROM A PREVIOUS FIGURE, REPRESENTS EFFECT OF PRIOR STRESSLESS CORROSION OF STEELS IN CARBONATE WATER FOR 10 DAYS. (McADAM)
A
EFFECT OF NOTCHES IN CARBON STEELS AND ORDINARY ALLOY STEELS.
INVESTIGATION BY P. LUDWIK AND SCHEU
d=0.2mm, r=0.05mm, d/r=4.0
THEORETICAL DECREASE IN FATIGUE LIMIT FOR d/r=4.0
THE CURVES, TRANSFERRED FROM A PREVIOUS FIGURE, REPRESENT EFFECT OF PRIOR STRESSLESS CORROSION IN CARBONATE WATER. (McADAM)
▽— CHROME-NICKEL TUNGSTEN STEELS.
□— CHROME-VANADIUM STEELS.
●— CHROME-SILICON STEELS.
△— CHROME-COPPER STEELS.
◇— CHROME-NICKEL STEELS.
○— SILICON STEELS.
×— CARBON STEELS.
STEELS 200 DAYS
STEELS 50 DAYS
STEELS 25 DAYS
STEELS 10 DAYS
B
EFFECT OF NOTCHES IN ALUMINUM ALLOYS
INVESTIGATION BY P. LUDWIK AND SCHEU.
d=0.2mm., r=0.05mm.
○—ALUMINUM ANNEALED.
△—ALUMINUM ALLOY.
▲—ALUMINUM ALLOY HARDENED AND COLD DRAWN
N
L
M
STEELS d/r=28.4 (McADAM)
STEELS d/r=4.0 (LUDWIK'S DATA)
C
INVESTIGATION BY R.R. MOORE
d=0.038 IN., r=0.010 IN
●—ALUMINUM COLD DRAWN
□—DURALUMIN
EFFECT OF NOTCHES IN MAGNESIUM ALLOYS.
INVESTIGATION BY R.R MOORE.
d=0.038mm, r=0.010mm.
●—MAGNESIUM EXTRUDED.
○—MAGNESIUM ALLOY EXTRUDED.
STEELS d/r=28.4 (McADAM)
STEELS d/r=4.0 (LUDWIK'S DATA)
D
PERCENTAGE DECREASE IN FATIGUE LIMIT DUE TO NOTCH
TENSILE STRENGTH, LB. PER SQ. INCH (THOUSANDS)

FIGURE 9.—*Relation between tensile strength and percentage damage due to notches in various metals and alloys.*

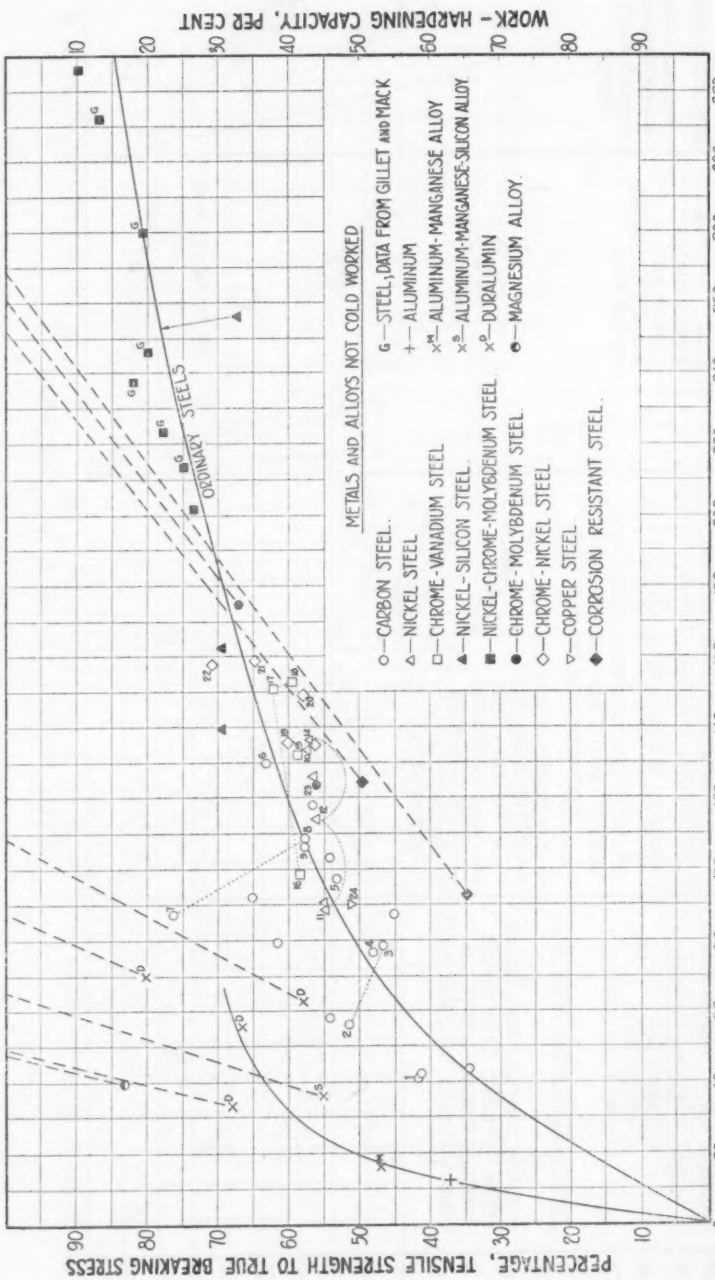

FIGURE 10.—*Relation between tensile strength and tensile work-hardening capacity, as influenced by composition and heat treatment.*

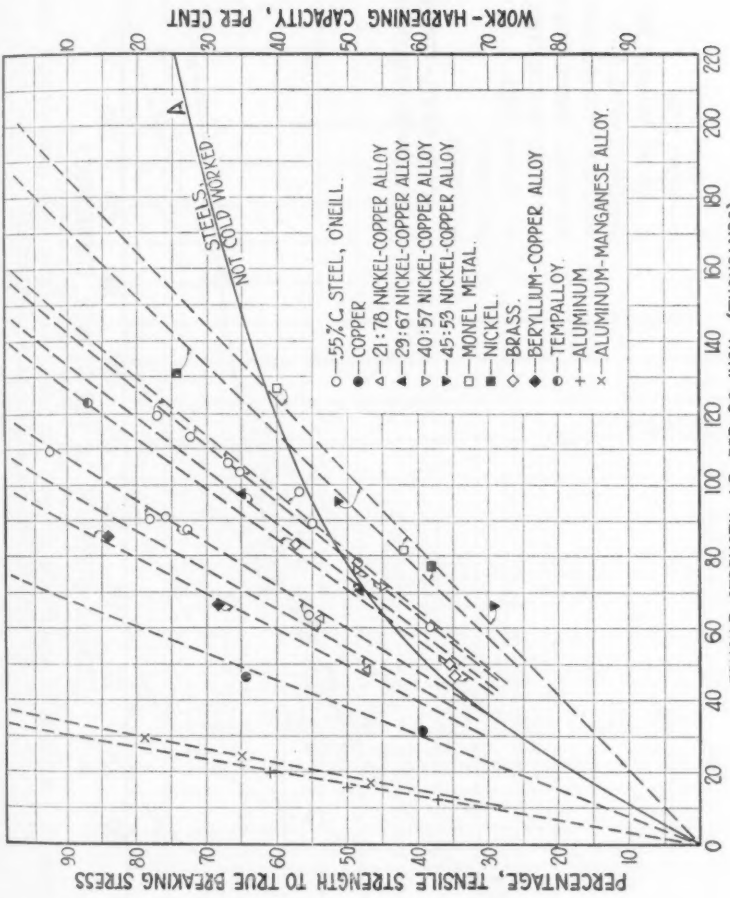

FIGURE 11.—*Relation between tensile strength and tensile work-hardening capacity, as influenced by cold working.*

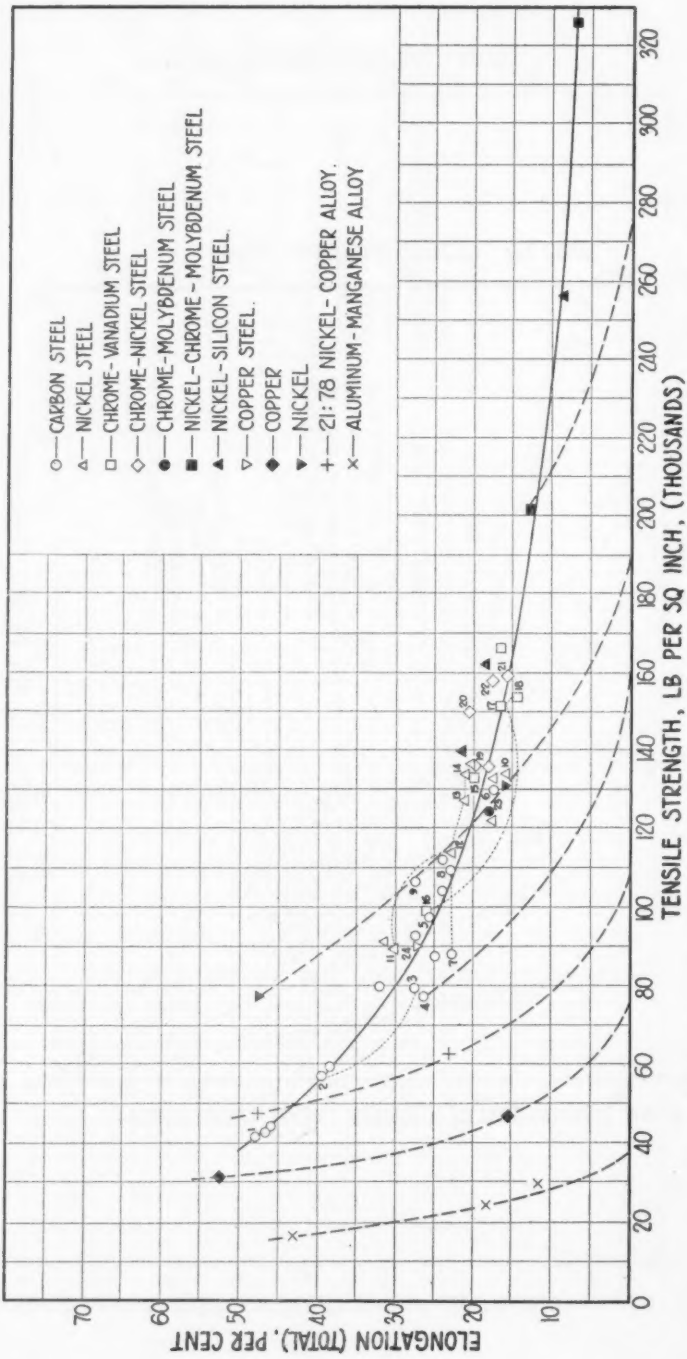

FIGURE 12.—*Relation between tensile strength and total tensile elongation* (percent in 2 inches).

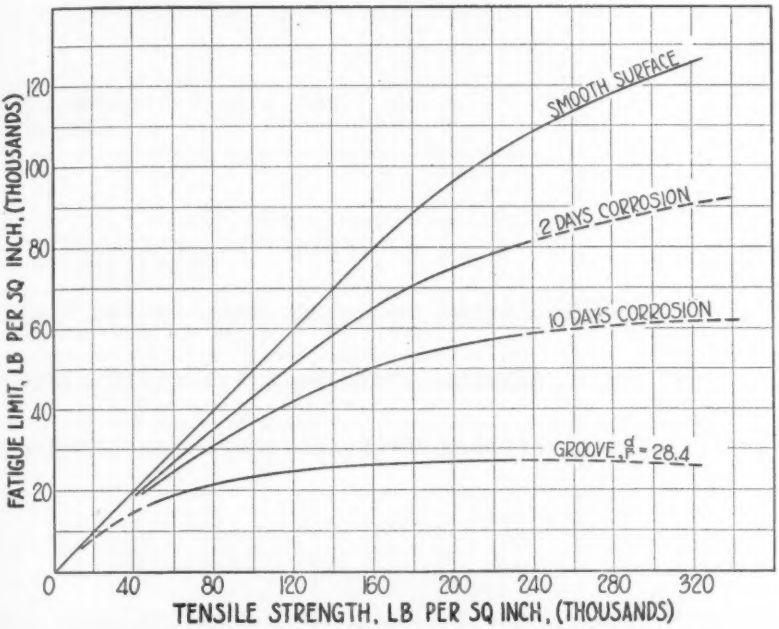

FIGURE 13.—*Loss of advantage of superior strength due to notches.*

TABLE 1.—*Chemical composition*

Material[a]	Composition (percent)													
	Designation	C	Mn	Si	Cv	V	Ni	Mo	Cu	Zn	Sn	Al	Mn	Fe
Ingot iron	EK	0.032	0.025	0.003										
Do	IZ	.018	.016	.002										
0.24 percent C Steel	EL	.24	.4	.023										
Do	IH	.24	.57	.006										
0.26 percent C steel	EN	.26	.57	.06										
0.29 percent C steel	IX	.28	.54	.01										
0.36 percent C steel	AT	.36	.55	.3	0.014			0.06						
Do	AG	.36	.61	.019										
0.46 percent C steel	JR	.46	.65	.016										
0.49 percent C steel	AE	.49	.41	.23										
0.56 percent C steel	JA	.56	.67	.12										
1.09 percent C steel	EM	1.09	.33	.28										
3½ percent Ni steel	EJ	.32	.6	.21			3.47							
Do	LQ[b]													
3.7 percent Ni steel	IW	.28	.5	.19	.26		3.7							
5 percent Ni steel	CA	.52	.41	.32			5.37							
Chromium-vanadium steel	AU	.34	.71	.21	1.05	0.17								
Do	AZ	.46	.69	.24	.88	.14								
Do	AR	.50	.70		.99	.16								
Chromium-nickel steel	BC	.28	.69	.21	.73		1.51							
Do	AH	.39	.69	.17	.82		1.67							
Do	BW	.39	.57	.19	.92		1.83							
Do	AY	.43	.60	.21	.95		2.16							
Do	AX	.36	.48	.22	1.55		3.26							
Chromium-molybdenum steel	AL	.33	.71	.13	.95			.15						
Nickel-chromium-molybdenum steel	KO	.49	.64	.23	.94		1.93	.37						
Nickel-silicon steel	HG	.47	.87	1.58	.32		3.11							
Copper steel	IK	.27	.47	.01					0.82					
Stainless iron	GR	.12	.40	.18	12.67		.45		.05					
Do	GN	.13	.05	.22	13.35		.08		.45					
Do	GO	.08	.18	.23	12.20		.18		.13					
Do	FH	.11	.04	.10	11.84		.07		.94					
Stainless steel	FJ	.33	.08	.09	11.54		.08		.84					
Do	GS	.38	.26	.20	14.50		.23		.07					
Corrosion-resistant steel	EX	.80	.86	1.70	19.01		12.19		.05					
Do	EW	.38	.71	2.36	15.95		15.88		.08					
Do	EV	.39	.66	.144	17.71		25.25		.012					
Do	EU	.70	.72	3.08	17.32		25.81		.05					
Do	ES	.24	.80	1.65	5.42		22.90		.78					
Do	ET	.45	.49	1.39	8.38		28.20		.67					
Copper, electrolytic, HR	EE													0.004
Copper, electrolytic, CW	HU													.008
21-78 nickel-copper alloy, CW	HE	.031	.29	.005			21.24		77.92					.51

21:78 nickel-copper alloy, CW	HE	.031	.29	.005			21.24		77.92					.51
29:67 nickel-copper alloy, CR	HZ	.040	1.35	.002			28.66		67.11					2.82
40:57 nickel-copper alloy, HR	EH	.160	1.77	.06			40.29		56.63					1.09
Constantan, CR	HP	.04	1.03	.02			45.00		53.54		None			.38
Monel metal, CR	EP	.159	.95	.05			67.51		29.54					1.76
Nickel, CR	EO	.098	.03	.09			98.96		.17					.57
Nickel-copper-zinc alloy, CD	CG						10.89		60.08	29.05				
Ambrac, HR	CD		.75				19.75		74.01	5.17				
Copper-nickel-tin alloy, CD	CF						29.08		69.82		.95			
92:8 copper-tin alloy, CD	EDA								91.78		8.20			.07
90:10 copper-tin alloy, CD	EC-12						.13		89.41		10.49			.07
Do	ECA													
71:28:1 copper-zinc-tin alloy	MA		None	.003					70.64	28.18	1.17			.01
65:35 copper-zinc alloy, CD	EG								64.95	35.06				.04
Aluminum bronze	KE								90.39			10.00		.17
Do	BJB								90.52			10.01		.002
Copper-nickel-silicon alloy	KBA			.82			3.27		95.96					.087
Aluminum, A	DR		.005	.22					.12			99.35		.30
Aluminum, ½ HT	DRA		.005	.22					.12			99.35		.30
Aluminum, HT	DRB		.005	.22					.12			99.35		.30
Alluminum-manganese alloy, A	DS		1.22	.35					.16			97.98		.29
Aluminum-manganese alloy, ½ HT	DSA		1.22	.35					.16			97.98		.29
Aluminum-manganese alloy, HT	DSB		1.22	.35					.16			97.98		.29
Do	JS		1.35	.16					.15			97.76		.59
Duralumin, T	KI		.72	.36					4.37			93.31	.55	.69
Do	GU		.55	.29					4.10			93.86	.63	.57
Do	LG		.58	.40					4.04			93.95	.35	.68
Duralumin	DU		.60	.37					4.18			93.89	.92	.54
Duralumin, T	DUA		.60	.37					4.18			93.89	.92	.54
Do	GT		.50	1.02					3.72			94.06	.28	.42
Do	KA		.63	.21					4.26			93.60	.63	.67
Do	JU		.52	.18					4.14			93.37	.62	1.17
Aluminum-copper alloy	DVA		.82	.82					4.55			Rem.		.56
Aluminum-magnesium-silicon alloy	DTA		.006	.56					.15			98.19	.55	.54
Do	DTB		.006	.56					.15			98.19	.55	.54
Magnesium-aluminum alloy	CN		.002	.01						None	None	4.40	95.91	.15

[a] HR, hot rolled; CW, cold worked; CR, cold rolled; CD, cold drawn; A, annealed; T, tempered; HT, hard temper; ½ HT, half-hard temper.
[b] About the same in composition as IW.

TABLE 2.—*Details of mechanical and thermal treatment*

Comparison number	Material [a]	Designation	Heat treatment					
			Temperature	Time held	Cooled in	Temperature	Time held	Cooled in
			°F	Min		°F	Min	
	Ingot iron	EK-17.5	1,750	30	Furnace			
	do	EK-W-7	1,750	45	Water	700	120	Furnace.
1	do	IZ-17.5	1,750	45	Furnace			
	0.24-percent C steel	EL-16.5	1,650	60	do			
2	do	IH-16.5	1,650	60	do			
3	do	IH-W-9	1,650	60	Water	900	120	Air.
	0.26-percent C steel	EN-W-9	1,650	60	do	900	120	Furnace.
4	0.29-percent C steel	IX-W-9	1,650	60	do	900	120	Air.
5	0.36-percent C steel	AT-W-10	1,550	60	do	1,000	120	Furnace.
	do	AG-15.5	1,550	60	Furnace			
	do	AG-W-9	1,550	60	Water	900	120	Do.
6	0.46-percent C steel	JR-W-10	1,500	60	do	1,000	120	Do.
	0.49-percent C steel	AE						
	do	AE-W-10	1,500	60	Water	1,000	120	Do.
7	0.56-percent C steel	JA-15	1,500	60	Furnace			
8	do	JA-W-11.75	1,500	60	Water	1,175	60	Do.
9	1.09-percent C steel	EM-14.75	1,475	60	Furnace			
	3½-percent Ni steel	EJ-14.5	1,675	60	Air	1,450	60	Do.
	do	EJ-W-10 [b]	1,450	60	Water	1,000	120	Do.
10	do	LQ-W-10	1,450	60	do	1,000	120	Do.
11	3.7-percent Ni steel	IW-14.5	1,450	60	Furnace			
12	do	IW-W-11 [c]	1,450	60	Water	1,100	120	Do.
13	do	IW-W-10 [c]	1,450	60	do	1,000	120	Do.
14	do	IW-W-9 [c]	1,450	60	do	900	120	Do.
	5-percent Ni steel	CA-14.25	1,425	60	Furnace			
15	Chromium-vanadium steel	AU-O-10 [d]	1,575	60	Oil	1,000	60	Do.
16	do	AZ-15.75 [d]	1,575	60	Furnace	Previously heated to 1,700° F. for 60 min. cooled in air.		
17	do	AZ-O-10 [d]	1,575	60	Oil	1,000	60	Furnace.
18	do	AZ-O-7.5 [d]	1,575	60	do	750	60	Do.
	do	AR	1,575	60	do	1,000	60	Do.
19	Chromium-nickel steel	BC-W-10	1,550	60	Water	1,000	120	Do.
	do	AH	Heat treated airplane crank shaft material.					
20	do	BW-W-10	1,550	60	Water	1,000	120	Furnace.
21	do	AY-W-10	1,550	60	do	1,000	120	Do.
22	do	AX-W-10	1,550	60	do	1,000	120	Do.
23	Chromium-molybdenum steel.	AL-O-10	1,575	60	Oil	1,000	60	Do.
	Nickel-chromium-molybdenum steel.	KO-O-8	1,600	60	do	800	60	Air.
	do	KO-O-3.5	1,600	60	do	350	60	Do.
	Nickel-silicon steel	HG-14.75	1,475	60	Furnace			
	do	HG-O-10	1,500	60	Oil	1,000	60	Do.
	do	HG-O-7.5	1,500	60	do	750	60	Do.
24	Copper steel	JK-W-9	1,600	60	Water	900	120	Furnace.
	Stainless iron	GR	Heat treated by manufacturer.					
	do	GN-W-12	1,800	90	Water	1,200	120	Air.
	do	GO-18	1,800	120	Furnace			
	do	GO-W-12	1,800	60	Water	1,200	120	
	do	FH-16	1,600	120	Furnace			
	Stainless steel	FJ-17	1,700	120	do			
	do	GS-17	1,700	120	do			
	do	GS-O-12	1,800	60	Oil	1,200	120	Do.
	do	GS-O-10.75	1,800	60	do	1,075	120	Do.
	Corrosion-resistant steel	EX						
	do	EW						
	do	EV						
	do	EU						
	do	ES						
	do	ET						
	Copper, electrolytic, HR	EE-12	1,200	60	Furnace			
	Copper, electrolytic, CW	HU-2.5	250	180	do			
	21:78 nickel-copper alloy, CW.	HE-14	1,400	60	do			
	do	HE-4	400	180	do			
	29:67 nickel-copper alloy, CR.	HZ-14.5	1,450	60	do			

[a] HR, hot rolled; CW, cold worked; CR, cold rolled; CD, cold drawn; A, annealed; T, tempered; ½ HT, half hard temper; HT, hard temper; when no heat treatment is listed, material was tested as received.

[b] Previously heated to 1675° F for 30 min, cooled in air.

[c] Previously heated to 1675° F for 60 min, cooled in air.

[d] Previously heated to 1700° F for 60 min, cooled in air.

TABLE 2.—*Details of mechanical and thermal treatment*—Continued

Comparison number	Material	Designation	Heat treatment					
			Temperature	Time held	Cooled in	Temperature	Time held	Cooled in
			°F	Min		°F	Min	
	29:67 nickel-copper alloy, CR.	HZ-8.5	850	180	Furnace			
	40:57 nickel-copper alloy, HR.	EH-14	1,400	60	do			
	do	EH						
	Constantan, CR	HP-12	1,200	60	Furnace			
	do	HP-7.5	750	180	do			
	Monel metal, CR	EP-14	1,400	60	do			
	do	EP-8	800	180	do			
	Nickel, CR	EO-14	1,400	60	do			
	do	EO-6	600	120	do			
	Nickel silver, CD	CG						
	92:8 copper-tin alloy	EDA-12	1,200	60	Furnace			
	92:8 copper-tin alloy, CD	EDA						
	90:10 copper-tin alloy, CR	EC-12	1,200	60	Furnace			
	do	ECA						
	71:28 copper-zinc alloy	MA						
	65:35 copper-zinc alloy, CD.	EG-12	1,200	60	Air			
	do	EG-4.5	450	60	do			
	Aluminum bronze	KE						
	do	KE-6	600	180	Furnace			
	do	BJB-11						
	Copper-nickel-silicon alloy	KBA-8	Hard drawn rods heat treated. Final heat treatment, 2 hours at 797° F.					
	Beryllium copper, CR	MT-14.25-W	1,425		Water	Previously cold rolled 25 percent, as received.		
	do	MT-4.5	T.450	Previously cold rolled 25 percent, as received.				
	Aluminum, A	DR						
	Aluminum, ½ HT	DRA						
	Aluminum, HT	DRB						
	Aluminum-manganese alloy, A.	DS						
	Aluminum-manganese alloy, ½ HT.	DSA						
	Aluminum-manganese alloy, HT.	DSB						
	do	JS	Heat treated by manufacturer.					
	Duralumin, T	KI	Do.					
	do	GD	Do.					
	do	LG	Do.					
	Duralumin	DU	Annealed by manufacturer.					
	Duralumin, T	DUA	Heat treated by manufacturer.					
	do	GT	Do.					
	Duralumin	KA	Do.					
	do	JU	Do.					
	Aluminum-copper alloy, ½ HT.	DVA	Do.					
	Aluminum-manganese-silicon alloy.	DTA	Do.					
	do	DTB	Do.					
	Magnesium-aluminum alloy.	CN						

TABLE 3.—*Physical properties*

NOTES

"*Proof stress*" is the stress that, after release of load, will cause permanent elongation of 0.0001 in. per inch length. "*Elastic limit*" is the highest stress that, after release of load, will cause no appreciable permanent elongation. "*Proportional limit*" is the highest stress that will not cause appreciable departure from a linear stress-strain relationship. (The smallest divisions of the extensometer scale were 0.0001, but estimate could be made to 0.00002 in. The extensometer was of a type that permitted accurate determination of permanent set.) "*True breaking stress*" is the actual breaking load divided by the reduced area at fracture.

Comparison no.	Material	Condition [a]	Designation	Tensile strength (TS) [b]	Johnson's limit [b]	Proof stress (PS) [b]	Elastic limit [b]	Proportional limit [b]	Elongation in 2 inches [b]	Reduction of area [b]	Endurance limit	True stress at maximum load	True breaking stress (TBS)	Elongation at maximum load	Percentage ratio PS to TBS	Percentage ratio TS to TBS
				lb/sq in.	*lb/sq in.*	*lb/sq in.*	*lb/sq in.*	*lb/sq in.*	*Percent*	*Percent*	*lb/sq in.*	*lb/sq in.*	*lb/sq in.*	*Percent*	*Percent*	*Percent*
------	Ingot iron	A	EK-17.5	42,500	15,000	16,000	14,000	14,000	46.5	71.5	21,000	49,700	105,000	16.95	15.5	41.25
------	------do	WQ and T	EK-W-7	44,000	22,000	22,500	21,000	20,000	46.0	75.0	24,000	52,400	128,000	19.1	17.6	34.35
1	------do	A	IZ-17.5	41,500	17,000	17,000	17,000	16,000	48.0	73.6	24,000	52,500	100,000	26.5	17.0	41.50
------	0.24 percent C steel	A	EL-16.5	50,300	32,000	33,000	32,000	31,000	58.5	58.5	27,000	71,000	109,000	19.78	30.5	54.2
2	------do	A	IH-16.5	56,700	40,000	40,000	28,000	26,000	39.5	61.3	24,000	67,200	110,000	17.82	36.35	51.5
3	------do	WQ and T	IH-W-9	79,000	60,000	58,000	57,000	50,000	27.5	67.9	37,000	89,600	169,700	12.6	34.2	46.5
------	0.26 percent C steel	WQ and T	EN-W-9	87,500	60,000	60,000	55,000	50,000	25.0	62.5	39,000	97,800	195,400	11.74	31.0	45.2
4	0.29 percent C steel	WQ and T	IX-W-9	77,000	52,000	52,000	50,000	50,000	26.5	66.9	38,500	86,200	159,800	11.96	32.5	48.1
5	0.36 percent C steel	WQ and T	AT-W-10	97,500	71,000	71,500	70,000	70,000	25.5	60.4	42,000	108,800	183,500	11.73	39.0	53.25
------	------do	A	AG-15.5	79,500	48,000	47,500	47,000	35,000	32.0	49.0	----------	92,000	129,000	15.65	36.8	61.6
------	------do	WQ and T	AG-W-9	103,500	75,000	75,500	75,000	60,000	24.0	59.5	----------	113,900	191,000	10.0	39.5	54.2
6	0.46 percent C steel	WQ and T	JR-W-10	129,800	100,000	101,400	99,500	92,300	17.5	51.9	59,000	138,300	205,400	6.5	49.5	63.2
------	0.49 percent C steel	AR	AE	92,300	57,000	59,000	57,000	----------	27.5	43.5	----------	108,400	141,500	17.16	41.7	65.2
------	------do	WQ and T	AE-W-10	111,800	76,000	77,000	76,000	63,000	24.0	56.0	53,000	122,500	197,600	10.43	38.95	56.6
7	0.56 percent C steel	A	JA-15	87,400	36,500	37,000	36,000	32,500	23.0	29.2	43,000	100,600	114,500	15.22	32.3	76.3
8	------do	WQ and T	JA-W-11.75	109,400	----------	----------	----------	----------	23.0	58.5	54,000	119,300	189,700	9.13	----------	57.65
9	1.09 percent C steel	A	EM-14.75	106,500	63,000	63,500	63,000	53,000	27.5	52.0	42,500	122,300	184,700	14.48	34.4	57.7
------	3½ percent Ni steel	A	EJ-14.5	90,800	60,000	61,000	55,000	48,000	31.5	58.5	49,000	96,700	164,000	6.52	37.2	55.3
------	------do	WQ and T	EJ-W-10	126,100	107,000	107,500	107,000	80,000	21.0	64.0	69,000	134,400	223,000	6.96	48.2	56.6
10	------do	WQ and T	LQ-W-10	133,700	121,300	123,300	121,300	106,400	21.0	63.8	----------	140,900	233,000	5.44	52.9	57.4
11	3.7 percent Ni steel	A	IW-14.5	89,250	59,000	60,000	59,000	47,500	30.0	59.2	49,000	114,400	165,400	15.2	36.3	54.95
12	------do	WQ and T	IW-W-11	114,000	100,000	101,000	97,500	90,000	23.0	64.4	----------	122,700	202,800	7.61	49.8	56.2
13	------do		IW-W-10	128,100	114,000	114,600	110,000	94,300	20.6	61.8	----------	----------	----------	----------	----------	----------
14	------do	WQ and T	IW-W-9	136,000	122,000	123,000	115,000	105,000	20.5	61.5	----------	142,600	238,000	4.78	51.7	57.2
------	5 percent Ni steel	A	CA-14.25	122,000	55,000	55,000	45,000	45,000	17.5	24.0	55,000	136,800	155,200	12.6	----------	----------
------	------do	WQ and T	CA-W-11	133,000	95,000	95,000	80,000	80,000	17.5	39.0	66,000	144,300	185,000	8.26	----------	----------
15	Chromium-vanadium steel	OQ and T	AU-O-10	132,200	111,000	114,500	112,500	100,000	20.0	60.9	68,500	139,500	224,200	5.48	51.1	58.9
16	------do	A	AZ-15.75	98,800	55,000	55,000	40,000	40,000	26.0	51.1	42,000	114,400	169,400	7.65	32.45	58.3
17	------do	OQ and T	AZ-O-10	151,000	122,500	125,000	115,000	90,000	16.5	53.7	69,000	161,400	243,000	6.82	51.45	62.1
18	------do	OQ and T	AZ-O-7.5	153,500	115,000	117,500	100,000	82,500	14.5	54.2	78,000	162,500	250,000	5.83	45.6	59.5
------	------do	OQ and T	AR-O-10	166,500	162,500	162,500	150,000	115,000	15.5	51.1	85,000	181,000	305,000	8.7	53.3	54.6
19	Chromium-nickel steel	WQ and T	BC-W-10	135,900	119,100	121,700	119,100	111,500	20.0	62.2	68,000	143,700	225,800	5.22	53.95	60.2

------	------do	AR	AH	135,400	112,500	117,000	107,500	90,000	18.0	54.9	66,500	149,500	238,800	10.43	49.0	56.7
20	------do	WQ and T	BW-W-10	149,400	132,500	135,000	125,000	120,000	20.5	62.2	75,000	156,500	258,000	4.82	52.35	57.9
21	------do	WQ and T	AY-W-10	159,000	143,100	144,200	135,200	103,400	15.5	52.0	76,000	165,000	245,200	4.81	58.8	64.8
22	------do	WQ and T	AX-W-10	157,700	141,000	142,000	139,000	115,000	17.5	50.7	89,500	160,500	222,000	5.22	64.0	71.0
23	Chromium-molybdenum steel.	OQ and T	AL-O-10	124,500	94,000	95,000	90,000	78,000	18.0	64.0	58,500	136,100	221,400	9.35	42.9	56.25
------	Nickel-Chromium-molybdenum steel.	OQ and T	KO-O-8	201,500	165,000	170,000	165,000	132,500	13.0	43.7	------	210,700	274,200	4.56	62.0	73.5
------	------do	OQ and T	KO-O-3.5	326,000	91,900	78,000	65,000	62,800	7.0	11.5	------	346,000	362,000	6.09	21.5	90.0
------	Nickel-silicon steel	A	HG-14.75	139,500	76,000	77,000	70,000	40,000	21.5	43.0	65,000	156,300	200,400	10.78	38.4	69.6
------	------do	OQ and T	HG-O-10	162,500	115,000	115,000	100,000	90,000	18.5	46.5	89,000	174,800	233,700	7.52	49.2	69.6
------	------do	OQ and T	HG-O-7.5	256,000	210,000	212,000	204,000	170,000	8.5	47.0	108,000	260,000	377,500	1.5	56.2	67.8
24	Copper steel	WQ and T	JK-W-9	90,000	67,500	67,500	67,500	55,000	27.0	63.6	49,500	101,750	175,400	13.04	38.5	51.3
------	18-8 alloy	AR	LZ	92,900	20,100	21,600	15,100	12,600	65.5	74.5	------	147,350	268,000	58.7	8.1	34.65
------	Stainless iron	AR	GR	112,000	79,000	80,500	70,000	65,000	23.5	66.5	53,500	114,000	210,000	5.7	38.3	53.35
------	------do	WQ and T	GN-W-12	120,200	81,000	82,000	71,000	66,000	23.0	64.5	59,000	127,300	228,400	7.4	35.9	52.6
------	------do	A	GO-18	61,500	25,000	25,000	19,000	15,000	40.0	69.5	39,000	73,600	132,800	18.7	18.8	46.3
------	------do	WQ and T	GO-W-12	92,500	60,000	60,000	50,000	45,000	24.0	71.5	49,000	99,000	187,700	6.09	32.0	49.2
------	------do	A	FH-16	79,800	41,000	42,000	38,000	36,000	32.5	66.0	39,000	90,400	161,900	13.92	25.95	49.3
------	Stainless steel	A	FJ-17	96,800	42,000	42,000	38,000	35,000	28.0	61.0	52,000	109,700	183,000	13.5	22.9	52.8
------	------do	A	GS-17	96,000	43,000	41,000	40,000	40,000	32.0	60.2	------	109,800	174,600	14.4	23.5	54.9
------	------do	OQ and T	GS-O-12	112,100	49,000	50,000	43,000	38,000	23.5	56.0	53,500	126,200	208,000	13.7	24.0	53.9
------	------do	OQ and T	GS-O-10.75	179,000	130,000	123,000	100,000	85,000	11.0	38.5	------	186,900	234,000	4.35	52.1	76.5
------	Corrosion-resistant steel	AR	EX	124,000	45,000	42,500	33,000	30,000	22.5	27.0	65,000	146,000	161,700	17.82	26.3	76.7
------	------do	AR	EW-17	127,500	53,000	45,000	35,000	35,000	26.0	38.0	64,000	------	------	------	------	------
------	------do	AR	EV	114,300	50,000	50,000	40,000	30,000	23.0	35.5	54,000	131,500	160,300	15.08	31.2	71.3
------	------do	AR	EU	110,000	47,500	45,000	37,000	32,000	27.0	38.0	57,000	129,600	161,200	17.82	27.9	68.3
------	------do	AR	ES	98,800	35,000	38,000	35,000	35,000	33.0	59.0	50,000	117,500	187,800	19.31	24.0	52.6
------	------do	A	ET-17	113,000	46,000	49,000	45,000	30,000	23.5	37.5	------	132,800	168,000	17.4	29.1	67.2
------	------do	AR	ET	124,800	75,000	50,000	40,000	25,000	28.0	59.5	58,000	140,900	251,400	7.6	19.9	49.7
------	Copper	A	EE-12	31,200	------	4,500	3,000	------	52.5	73.5	10,000	42,200	79,300	35.2	5.7	39.3
------	------do	LA	HU-2.5	46,300	30,000	20,000	11,000	10,000	15.5	63.5	------	47,100	71,900	1.74	27.8	64.4
------	21:78 nickel-copper alloy	A	HE-14	48,000	11,000	10,200	7,500	6,200	47.5	73.5	17,800	62,900	101,800	31.1	10.0	47.1
------	------do	LA	HE-4	62,500	46,000	45,000	37,000	25,000	23.0	68.0	25,500	65,600	115,600	4.87	38.9	54.0
------	29:67 nickel-copper alloy	A	HZ-14.5	70,400	24,000	24,500	15,000	12,500	44.5	70.0	26,500	92,800	145,700	31.75	16.8	48.3
------	------do	LA	HZ-8.5	97,400	75,000	74,000	60,000	55,000	19.0	54.5	36,000	104,600	150,000	7.39	49.3	64.9
------	40:57 nickel copper alloy	A	EH-14	71,500	25,000	26,500	22,500	20,000	47.5	67.5	30,000	94,000	159,800	31.28	16.6	44.7
------	------do	AR	EH	76,100	47,000	45,000	36,000	32,000	32.5	62.0	32,500	92,400	156,000	21.3	28.85	48.75
------	Constantan	A	HP-12	66,000	22,000	22,500	21,000	20,000	47.5	78.5	30,000	86,800	227,700	31.5	9.9	29.1
------	------do	LA	HP-7.5	95,500	65,000	65,000	57,500	38,500	22.5	10.8	40,500	107,800	187,300	7.83	34.7	51.0
------	Monel metal	A	EP-14	81,900	33,000	33,000	20,000	28,000	48.5	73.0	36,000	108,300	195,300	32.36	16.9	41.9
------	------do	LA	EP-8	127,000	97,000	90,000	85,000	85,000	21.5	59.5	52,000	139,200	211,660	9.56	42.5	60.0
------	Nickel	A	EO-14	77,300	23,000	23,500	21,000	21,000	47.5	74.0	33,400	105,800	203,000	36.96	11.6	38.1
------	------do	LA	EO-6	130,800	91,000	85,000	80,000	80,000	16.5	35.5	50,400	145,500	175,700	11.3	48.3	74.7
------	Copper-nickel-zinc alloy	------	CG	58,800	29,000	32,000	25,000	14,000	50.0	58.0	------	81,250	125,000	38.3	25.6	47.0
------	Ambrac	HR	CD-14	51,100	------	13,000	9,000	------	47.5	72.9	------	68,500	135,200	33.9	9.6	37.8
------	------do	HR	CD	57,500	------	34,000	26,000	------	34.0	69.0	23,000	69,000	124,200	20.0	27.4	46.3
------	Copper-nickel-tin alloy	A	CF-15	58,000	------	16,500	12,000	------	33.0	51.5	22,500	75,600	110,400	30.4	14.9	52.5
------	------do	CD	CF	90,500	------	54,000	14,000	------	4.0	23.5	33,500	91,300	107,800	0.85	50.5	83.9
------	92:8 copper-tin alloy	A	EDA-12	56,500	20,500	20,500	19,000	18,000	81.0	73.0	21,000	93,200	153,600	65.05	13.3	36.8

[a] A, annealed; AR, as received; LA, low temperature anneal; OQ, oil quenched; T, tempered; WQ, water quenched.
[b] Usually the average for at least 4 specimens.

TABLE 3.—*Physical properties*—Continued

Comparison no.	Material	Condition	Designation	Tensile strength (TS)	Johnson's limit	Proof stress (PS)	Elastic limit	Proportional limit	Elongation in 2 inches	Reduction of area	Endurance limit	True stress at maximum load	True breaking stress (TBS)	Elongation at maximum load	Percentage ratio PS to TBS	Percentage ratio TS to TBS
				lb/sq in.	*lb/sq in.*	*lb/sq in.*	*lb/sq in.*	*lb/sq in.*	*Percent*	*Percent*	*lb/sq in.*	*lb/sq in.*	*lb/sq in.*	*Percent*	*Percent*	*Percent*
------	92:8 copper-tin alloy	AR	EDA	91,500	63,000	54,000	42,500	27,500	18.0	59.0	----------	92,800	179,200	1.3	30.15	51.0
------	90:10 copper-tin alloy	A	EC–12	63,500	17,500	18,500	17,000	15,000	76.0	72.0	20,500	102,500	175,000	61.75	10.6	36.25
------	do	AR	ECA	95,300	57,500	51,500	40,000	30,000	22.5	56.5	----------	105,200	173,500	10.43	29.7	54.9
------	71:28 copper-zinc alloy	AR	MA	50,600	12,400	14,400	11,200	8,800	71.0	71.5	----------	82,600	142,000	63.4	10.1	35.6
------	65:35 copper-zinc alloy	A	EG–12	47,000	11,000	11,000	10,000	9,000	71.0	73.0	18,000	77,100	135,000	64.0	8.15	34.8
------	do	LA	EG–4.5	83,000	65,000	60,000	40,000	32,500	15.0	61.0	24,800	85,800	144,800	3.2	41.4	57.3
------	Aluminum bronze	AR	KE	79,500	34,000	37,000	21,000	18,000	33.5	31.9	----------	100,800	115,200	26.8	32.1	69.0
------	do	LA	KE–6	74,000	31,000	34,200	29,000	28,000	18.5	25.6	28,000	86,850	98,750	17.38	34.6	75.0
------	do	A	BJB–11	62,000	----------	31,500	15,000	----------	25.0	24.0	----------	74,800	81,550	20.64	26.4	76.1
------	Tempalloy	AR	KBA	69,500	55,000	56,000	48,000	35,000	18.5	79.0	----------	70,800	178,600	1.09	31.3	38.9
------	do	LA	KBA–8	122,300	95,000	90,000	62,500	55,000	6.0	16.0	25,000	125,500	141,600	2.74	63.5	86.4
------	Beryllium bronze	WQ	MT–14.26–W	66,500	16,250	17,500	9,750	9,750	38.0	31.9	25,000	95,200	97,600	43.0	17.9	68.1
------	do	WQ and T	MT–W–4.5	85,000	42,500	41,000	35,000	33,500	18.0	21.3	----------	98,300	101,400	----------	40.4	83.8
------	Aluminum	A	DR	12,600	----------	----------	----------	----------	----------	----------	----------	----------	34,000	----------	----------	37.0
------	do	½ HT	DRA	16,000	13,000	12,000	7,500	7,500	25.0	75.0	7,300	16,700	32,000	4.78	37.5	50.0
------	do	HT	DRB	20,400	16,000	16,000	14,000	11,500	18.5	64.0	8,400	20,350	33,500	4.13	47.7	60.9
------	Aluminum - manganese alloy	A	DS	16,700	2,500	2,500	2,000	1,500	43.0	67.5	7,000	21,000	35,760	25.88	6.7	46.7
------	do	½ HT	DSA	24,600	18,000	17,000	12,000	8,500	18.0	58.0	10,100	26,400	38,100	3.82	44.6	64.6
------	do	HT	DSB	29,600	22,000	21,000	13,500	12,500	11.5	42.1	10,800	30,200	37,600	1.65	55.8	78.8
------	do		JS	28,500	17,000	17,500	10,000	9,000	10.0	34.1	10,700	29,300	36,300	2.8	48.3	78.5
------	do		KI	62,700	30,500	31,000	29,000	28,000	26.0	39.8	----------	74,700	94,200	19.1	32.9	66.6
------	Duralumin T	AR	GU	56,000	27,000	27,000	20,000	17,000	27.0	39.5	13,000	67,000	84,100	19.57	32.1	66.6
------	do		LG	57,400	29,000	29,600	27,000	26,000	24.5	41.0	----------	67,650	89,000	----------	33.3	64.5
------	do	AR	DU	33,300	20,000	20,000	18,000	15,000	18.0	42.5	13,500	36,400	49,200	9.31	40.7	67.6
------	do	T	DUA	62,500	30,000	29,000	23,000	13,000	31.0	46.0	----------	75,200	108,300	20.3	26.8	57.8
------	do	T	GT	70,100	45,000	45,000	40,000	36,000	19.0	26.0	16,700	80,200	87,800	14.35	51.2	79.8
------	do		KA	53,000	27,000	27,500	25,000	23,000	22.0	35.7	16,500	63,400	76,700	17.4	35.9	69.1
------	do		JU	53,300	26,000	26,500	25,000	22,000	25.5	41.3	16,500	62,800	79,700	17.8	33.2	66.9
------	do		DVA	59,000	30,000	30,000	25,000	19,000	23.5	41.2	----------	66,100	88,100	13.9	34.0	67.0
------	Aluminum-copper alloy		DTA	44,800	28,000	26,000	16,000	16,000	19.0	24.8	12,400	48,900	56,000	11.1	46.4	80.5
------	Aluminum - magnesium-silicon alloy	AR	DTB	36,000	13,000	14,000	9,500	6,000	37.5	56.0	12,100	45,300	65,700	25.86	51.25	54.8
------	do															
------	Magnesium-aluminum alloy	AR	CN	39,800	20,000	18,300	13,000	12,500	16.0	20.0	----------	44,000	47,900	10.0	38.2	83.1

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PROPERTIES OF GRAY CAST IRON AS AFFECTED BY CASTING CONDITIONS

By C. M. Saeger, Jr., and E. J. Ash

ABSTRACT

A report of a preliminary investigation to determine the effect of maximum heating temperatures on the physical properties of different types of cast iron is given in this paper. It describes the methods and results obtained in a study of three types of cast iron. Four heats, all melted in a high-frequency induction furnace, were made for each type of iron with maximum heating temperatures of 1,400, 1,500, 1,600, and 1,700° C, respectively. Four pairs of transverse test bars, each pair of a given diameter, were cast from each heat in a dry-sand mold and the following properties were determined: Transverse breaking load, deflection, modulus of rupture and modulus of elasticity, hardness, density and microstructure. The shrinkage and the running qualities of the irons were also investigated. The density-temperature relation in the liquid state for each of the three irons was not affected by the degree of superheat. The strength of a bar of a given diameter was found to depend on the maximum heating temperature. In two types of iron this maximum did not occur at the same maximum heating temperature for bars of different diameter. In the third type of iron, the transverse breaking strength increased progressively up to 1,600° C for bars of all diameters.

The running quality of the irons investigated was not materially affected by the maximum heating temperature, but was found to be a function of the liquidus temperature. For any two irons poured at the same temperature, the running quality was found to be better in the case of the iron having the lower liquidus temperature.

The microstructure of the 1.2-inch bars indicated that high strength is associated with relatively small graphite flakes and a pearlitic-sorbitic matrix.

Numerous investigators have shown that the strength of cast iron is a function of the amount and distribution of graphite, the optimum properties being obtained with a pearlitic or sorbitic ground mass in which the graphite is disseminated as small globular particles. Improvement in the strength of cast iron has been brought about by the control of composition, of melting and foundry practice, and by heat treatment of the castings.

This paper is a report on a preliminary study of the effect on the physical properties of three different types of iron, of heating the iron to various temperatures considerably above the melting range, and pouring at temperatures approximately 150° C above the liquidus. A more detailed account has been published in the Transactions of the American Foundrymen's Association, vol. 41, 449-468(1933).

For each of the irons at each of the 4 temperatures whose effect was studied, a set of 8 cylindrical transverse test bars 23 inches in

length were cast simultaneously in a dry-sand mold. (See fig. 1.) Each set consisted of 2 bars of each of the diameters 0.75, 1.2, 1.5, and 2.2 inches. The bars of 1.5-inch diameter were machined to a diameter of 1.2 inches before being tested to determine the "skin effect"; the others were tested in the as-cast condition. The cross-sectional areas of the bars as tested were, therefore, in the approximate ratio of 1:3:9.

The castings made in a three-part cylindrical flask were bottom poured, the bars being arranged so as to promote uniform cooling of the bars after casting. The internal surfaces of the mold, before drying in the oven, were blackened with a mixture of water, graphite, clay, and molasses to produce castings free from "burnt-on" sand. The green-sand cope, containing the pouring basin, was placed in position just before casting.

Each charge of approximately 225 lb of metal was melted in a high-frequency induction furnace of the tilting type in a crucible of commercial magnesia. The maximum heating temperatures were 1,400, 1,500, 1,600, and 1,700° C, respectively, for each type of iron. Temperatures of 1,600° C and below were measured by a platinum-to-platinum 10-percent rhodium couple, whereas an optical pyrometer was used for fixing the 1,700° C point.

After a charge of metal had attained the desired maximum temperature the power was cut off and the metal allowed to cool to approximately 150° C above the liquidus temperature of the stock pig iron used in that particular charge. It should be mentioned that the liquidus temperatures of the cast metal, shown in table 1, differed from those of the stock iron used. Having attained the desired pouring temperature, the metal was poured directly from the furnace into the transverse bar mold.

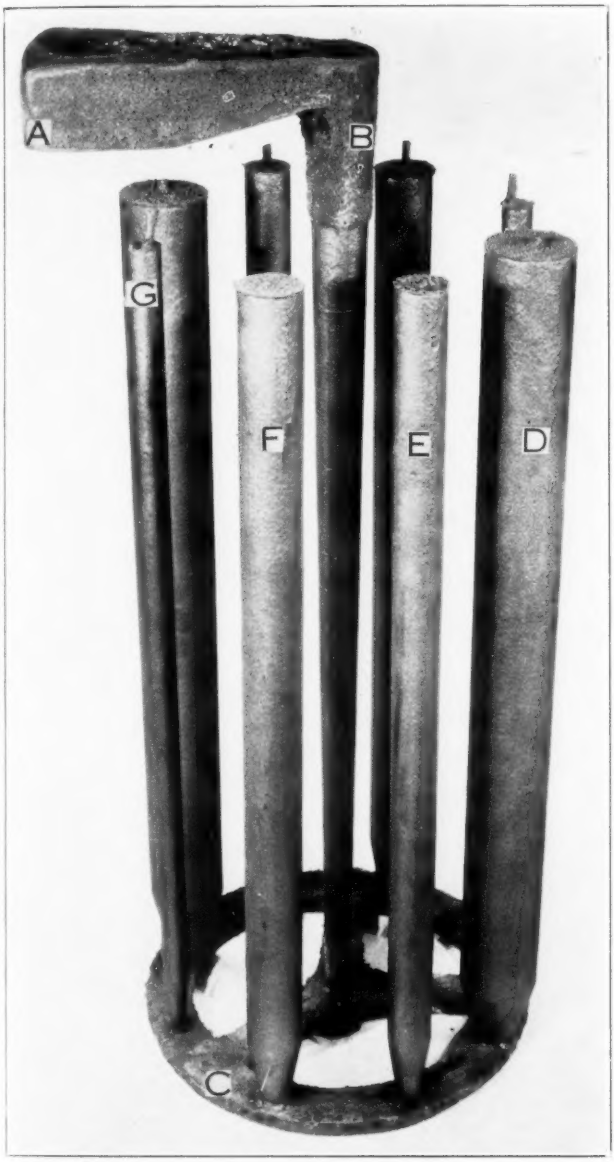

FIGURE 1.—*Casting showing the method of pouring bars for transverse tests.*

A, Pouring basin; *B*, down gate; *C*, feeding ring; *D*, 2.2 inch diameter bar; *E*, 1.2 inch diameter bar; *F*, 1.5 inch diameter bar; *G*, 0.75 inch diameter bar.

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TABLE 1.—*Composition and transverse properties of test bars of different diameters*

Iron	Cast or machined to size. C= cast; M= machined	Maximum heating temperature	Pouring temperature	Temperature of liquidus	Chemical composition, percent				Transverse test bar 0.75-inch diameter					Transverse test bar 1.2-inch diameter					Transverse test bar 2.2-inch diameter				
									Carbon content, percent			Breaking load	Deflection	Carbon content, percent			Breaking load	Deflection	Carbon content, percent			Breaking load	Deflection
					Si	S	Mn	P	Total carbon	Graphitic carbon	Combined carbon			Total carbon	Graphitic carbon	Combined carbon			Total carbon	Graphitic carbon	Combined carbon		
		°C	°C	°C								*Lb*	*In.*				*Lb*	*In.*				*Lb*	*In.*
A	C	1,400	1,300	1,170	2.65	0.021	0.20	0.86	3.71	2.79	0.92			3.57	2.81	0.76	1,480	0.23	3.56	2.79	0.77	8,810	0.18
	M	1,400	1,300	1,170	2.65	.021	.20	.86						3.60	2.77	.83	1,320	.27					
	C	1,500	1,300	1,170	2.44	.014	.23	.85	3.69	2.96	.73	510	0.15	3.67	2.99	.68	2,120	.25	3.66	3.00	.66	10,110	.18
	M	1,500	1,300	1,170	2.44	.014	.23	.85						3.67	2.99	.68	1,720	.28					
	C	1,600	1,300	1,155	2.70	.013	.21	.83	3.53	2.90	.63	560	.18	3.55	2.94	.61	1,690	.20	3.50	3.17	.33	8,680	.11
	M	1,600	1,300	1,155	2.70	.013	.21	.83						3.52	2.96	.56	1,600	.23					
	C	1,700	1,300	1,175	2.70	.015	.21	.86	3.45	2.65	.80	530	.19	3.44	2.67	.77	1,610	.20	3.46	2.68	.78	8,450	.15
	M	1,700	1,300	1,175	2.70	.015	.21	.86						3.46	2.66	.80	1,510	.27					
B	C	1,400	1,380	1,225	2.12	.019	.17	.65	2.95	2.14	.81	850	.22	2.95	2.19	.76	2,830	.25	2.92	2.20	.72	14,200	.14
	C	1,500	1,380	1,240	2.05	.028	.15	.66	2.88	2.08	.80	870	.23	2.91	2.08	.83	2,670	.23	2.83	2.08	.75	14,980	.18
	M	1,500	1,380	1,240	2.05	.038	.15	.66						2.90	2.09	.81	2,650	.26					
	C	1,600	1,380	1,240	2.03	.023	.17	.69	2.95	2.07	.88	720	.22	2.95	2.05	.90	2,710	.27	2.91	2.09	.82	13,640	.15
	M	1,600	1,380	1,240	2.03	.023	.17	.69						2.95	2.06	.89	2,660	.27					
	C	1,700	1,380	1,245	2.17	.023	.19	.72	2.82	1.99	.83	800	.20	2.80	1.88	.92	2,780	.22	2.78	2.00	.78	14,930	.14
C	C	1,400	1,300	1,185	1.17	.054	.54	.10	3.83	2.76	1.07	760	.29	3.84	3.12	.72	2,040	.30	3.81	3.07	.74	10,130	.22
	C	1,500	1,300	1,200	1.16	.055	.57	.10	3.77	2.51	1.26	810	.29	3.76	2.66	1.10	2,280	.22	3.73	2.77	.96	11,720	.20
	C	1,600	1,300	1,220	1.17	.055	.58	.12	3.65	1.14	2.51	860	.22	3.64	2.74	.90	2,590	.34	3.63	2.86	.77	11,960	.20
	C	1,700	1,300	1,215	1.16	.054	.62	.10	3.62	1.34	1.28	800	.15	3.60	2.76	.84	2,620	.28	3.59	2.34	.75	11,760	.16

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The transverse breaking load of the bars was determined with an Amsler universal testing machine of 50,000-lb capacity, the load being applied so as to give a uniform rate of deflection for all bars of approximately 0.02 inch in 10 seconds. An 18-inch span was used in breaking the 1.2- and 2.2-inch bars and a 15-inch span for the 0.75-inch bars. The transverse test data, together with the chemical composition and the temperature data are given in table 1. The effect of maximum heating temperature of the melt on the modulus of rupture and modulus of elasticity is shown in figure 2. However, for the purpose of brevity, data relating to specific-volume-temperature relation; linear contraction, density, hardness, and micrographs are omitted from this condensed paper. These data can be found in the original publication.[1]

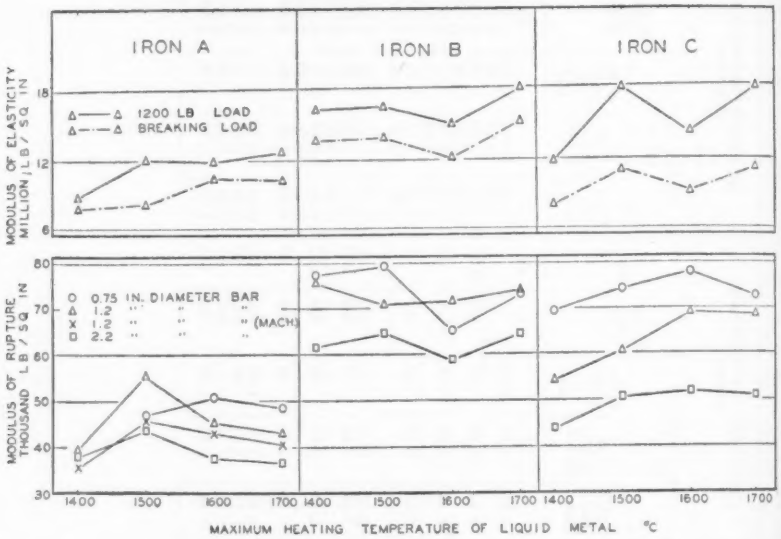
IRON A
IRON B
IRON C
MODULUS OF ELASTICITY MILLION LB / SQ IN
1200 LB LOAD
BREAKING LOAD
MODULUS OF RUPTURE THOUSAND LB / SQ IN
0.75 IN. DIAMETER BAR
1.2 " " "
1.2 " " " (MACH)
2.2 " " "
MAXIMUM HEATING TEMPERATURE OF LIQUID METAL °C

FIGURE 2.—*Modulus of rupture and modulus of elasticity as affected by maximum heating temperature.*

The moduli of elasticity in this figure are for the 1.2 inch diameter bar.

The running quality of each metal was determined by the method described by Saeger and Krynitsky [2] which consists essentially in casting a spiral strip of small cross section in no. 00 Albany green sand. The results are plotted in figure 3.

Microstructure. Cross sections perpendicular to the length of the 1.2-inch bars of the three irons (A, B, and C) were examined microscopically. The grinding and polishing of the specimens was done according to the method of Vilella [3] in order to preserve the graphite particles intact, and thus permit a comparison of the size of the graphite particles in the different irons.

The results of the investigation support the following essential conclusions:

[1] C. M. Saeger, and E. J. Ash. *Properties of gray cast iron as affected by casting conditions,* American Foundrymen's Transactions, **41**, 449-468(1933).

[2] C. M. Saeger, Jr., and A. I. Krynitsky, *A practical method for studying the running qualities of a metal cast in foundry molds.* Trans., A.F.A., **39**, 513-540(1931).

[3] J. R. Vilella, *Improved method of polishing metallographic specimens* of cast iron. Metals and Alloys, **3** 205(1932).

1. The density-temperature relation in the liquid state, for each of the three irons, was not affected by the degree of superheat.

2. The strength of a bar of a given diameter was found to depend on the maximum heating temperature. In two types of iron this maximum did not occur at the same maximum heating temperature for bars of different diameter. In the third type of iron, the transverse breaking strength increased progressively up to 1,600° C for bars of all diameters.

3. The running quality of the irons investigated was not materially affected by the maximum heating temperature, but was found to be a function of the liquidus temperature. For any two irons, poured at the same temperature, the running quality was found to be better in the case of the iron having the lower liquidus temperature.

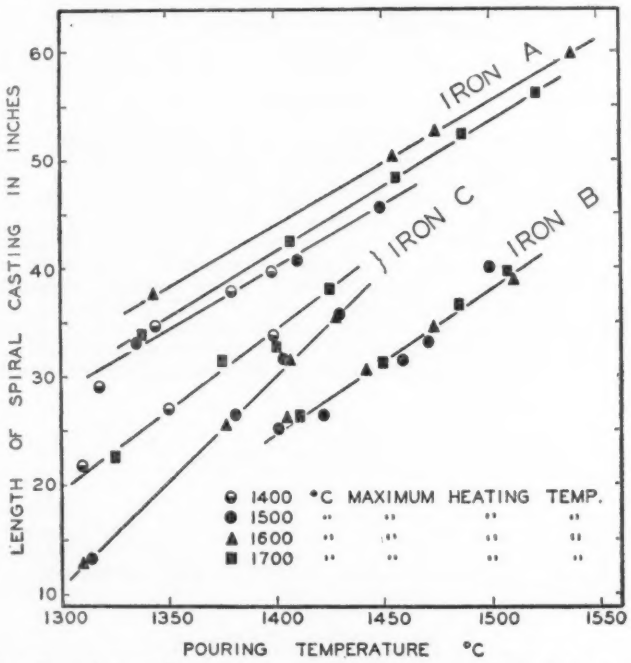

FIGURE 3.—*Running quality of irons* A, B, *and* C, *as affected by the maximum heating temperature and pouring temperature.*

4. Tests on the 1.5-inch bars machined to 1.2-inch diameter indicated that the removal of the "skin" lowered the transverse breaking strength considerably. The deflection value for the machined bar was, in general, greater than the deflection of the 1.2-inch bar as cast.

5. The microstructure of the 1.2-inch bars indicated that the irons of low strength contained relatively large straight graphite flakes and coarse pearlite, whereas the irons of high strength possessed a matrix of fine pearlite or sorbite with relatively small graphite flakes disseminated through it.

6. Although a simple relationship between transverse strength and the temperature of "super-heating" prior to casting has not been established the marked improvement attained in some cases suggests the desirability of further study along this line.

WASHINGTON, August 14, 1934.

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP727

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EFFECT OF MELTING CONDITIONS ON THE RUNNING QUALITY OF ALUMINUM CAST IN SAND MOLDS

By A. I. Krynitsky and C. M. Saeger, Jr.

ABSTRACT

The effect of maximum heating temperature on the running quality of liquid metal has been studied for 2 grades of aluminum and an aluminum—8 percent copper alloy. The running quality was measured in terms of the length of a spiral casting obtained by pouring the metal under carefully controlled conditions. The effect of various treatments of the metal was also investigated.

It was found that the relation between length of the spiral and the pouring temperature is linear. The running quality of the metals which had been heated to a maximum temperature of 850° C was in all cases less than when the metal had been heated to 750° C. Pure aluminum (99.8 percent) was found to have markedly higher running qualities than the commercial (99.2 percent) aluminum. The running quality of the aluminum—8 percent copper alloy—was not much different from that of commercial aluminum.

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I. INTRODUCTION

In a previous paper (1)[1] a practical method has been described for determining the running quality of metals. It consists essentially in pouring, under carefully controlled conditions, a spiral casting of relatively small cross section of the design shown in figure 1. The length of the spiral obtained under a given set of conditions is a numerical measure of the running quality of the metal under these conditions. The designation "good" running quality, or "high" running quality, are to be understood as indicating that the metal produced long spirals.

In making some experiments designed primarily to demonstrate the possibilities of the method, it had been observed that the running quality of commercial aluminum, poured at a given temperature, depended on the maximum temperature to which the metal had been

[1] Figures in parentheses here and throughout the text indicate references given in the "References" at the end of this paper.

superheated previous to pouring (1). In dry sand molds it was found that the lengths of the spirals, poured at a given temperature, were in the inverse order of the 3 maximum temperatures 750, 790, and 840° C to which the metal had been superheated. In green sand molds this order was not preserved exactly, the 840° C maximum heating temperature resulting in a spiral of length shorter than that obtained for 750° C and longer than that obtained for 790° C. The present work was undertaken to study this effect more systematically but had to be discontinued before completion. It is believed, however, that the results obtained, though incomplete and not entirely conclusive, will be of some interest.

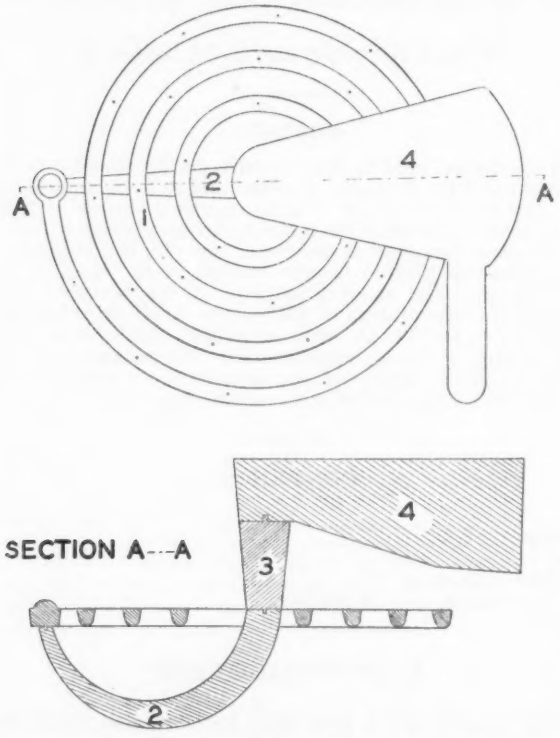

FIGURE 1.—*Spiral casting for determining the running quality of molten metals in a sand mold.*

1, Spiral; 2, hour gate; 3, down gate; 4, pouring basin and overflow

II. MATERIALS

Two grades of ingot aluminum, which will be designated as pure (Si 0.07, Fe 0.15, Cu 0.01, Al 99.8 percent) and commercial (Si 0.15, Fe 0.50, Cu 0.12, Al 99.2 percent) aluminum were used in this work and some tests were also made with an alloy of 8 percent copper with the commercial aluminum.

FIGURE 2.—*Immersed crucible apparatus for sampling the molten metal.*

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III. METHODS AND APPARATUS

A charge of 40 pounds of aluminum or of the aluminum-copper alloy was melted in a plumbago crucible in either a high-frequency induction furnace or in a gas-fired furnace. The molten metal was heated to a maximum temperature of either 750 or 850° C held at that temperature for 1 minute (except in the tests later referred to as "prolonged heating" in which the metal was held for 30 minutes at the maximum temperatures), and allowed to cool slowly.

The temperature was measured with a chromel-alumel thermocouple in a porcelain insulating tube and protected with a porcelain protection tube inside an iron secondary tube coated with alundum cement. The cold junctions were kept at 0° C and the emf measured with a portable potentiometer.

Prior to pouring the first casting, a sample of the molten metal at a known temperature was taken from the crucible by means of the graphite immersion device shown in figure 2. This device, containing the liquid sample, was then placed in a dry sand mold to secure a

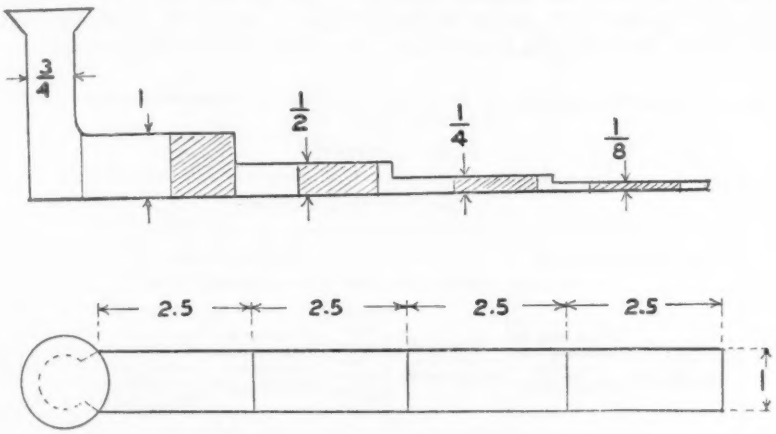

FIGURE 3.—*Stepped-bar casting.*

Shaded portions cut from bars were used in density determinations. All dimesnions are in inches.

slow rate of cooling. Longitudinal sections of the samples taken in this manner were deeply etched for visual examination.

The temperature of the metal in the crucible was then measured and a quantity of metal poured into a sand ingot mold to eliminate an excessive temperature drop due to contact with the cold lip of the crucible when pouring the test specimens. Two types of castings were poured, a spiral and the stepped-bar casting shown in figure 3. The metal was then allowed to cool until the next desired pouring temperature had been reached when another spiral and a stepped-bar casting were poured as before.

The stepped-bar castings were sectioned longitudinally and specimens for density determinations taken from one-half of the casting at the positions shown by the shaded sections of figure 3. The density determined on the half-inch section of the bar was considered to be representative of the metal cast. The remaining half of the stepped bar was deeply etched for visual examination.

All castings were made in green sand molds made of Albany 00 sand tempered to 6.0 to 7.0 percent of moisture. The molds were levelled and care was taken always to employ the same pouring height and rate.

In order to secure information which might throw some light on the cause of the behavior of aluminum which had been superheated, special treatments were given to a number of the melts. Some were treated with various amounts of zinc chloride which was introduced into the liquid metals by means of a small inverted graphite crucible. The side wall of the crucible was perforated to facilitate the reaction of the chloride and the molten metal. In other melts oxygen was passed for 5 minutes through the molten aluminum at 850° C to promote the formation of aluminum oxide. Finally, some tests were made using commercial aluminum which had been continuously exposed to the weather for a period of 75 days.

IV. RESULTS, CONCLUSIONS, AND DISCUSSION

The lengths of the spirals obtained under various conditions are plotted in figures 4, 5, and 6 while in table 1 are given selected values taken from the straight lines drawn through the plotted points.

TABLE 1.—*Running quality of pure and commercial aluminum and aluminum 8-percent copper alloy*

Pouring temperature	Lengths of spirals in inches													
	High frequency furnace				Gas-fired furnace									
	Untreated maximum temperature		Metal held for 30 minutes at maximum temperature		Untreated maximum temperature		Treated with oxygen at maximum temperature	Weather exposed ingots maximum temperature		Treated with zinc chloride				
										0.75% $ZnCl_2$ maximum temperature		0.50% $ZnCl_2$	0.25% $ZnCl_2$	
												maximum temperature		
	750° C	850° C	750° C	850° C	750° C	850° C	850° C	750° C	850° C	750° C	850° C	850° C		
°C														
PURE ALUMINUM														
700	14.1	11.4	------	------	13.3	12.5	11.8	------	------	12.7	12.0	------	------	
750	25.6	21.5	------	------	24.6	23.0	20.2	------	------	21.2	21.0	------	------	
COMMERCIAL ALUMINUM														
700	7.9	7.6	8.2	8.2	9.5	8.2	7.1	9.3	8.8	10.2	8.5	------	------	
750	15.0	14.8	15.4	15.4	18.0	15.8	15.3	18.5	17.0	18.8	16.8	------	------	
ALUMINUM-8 PERCENT COPPER ALLOY														
700	------	------	------	------	10.0	7.9	------	------	------	10.3	9.2	8.8	8.0	
750	------	------	------	------	18.4	15.4	------	------	------	17.5	17.0	16.8	15.6	

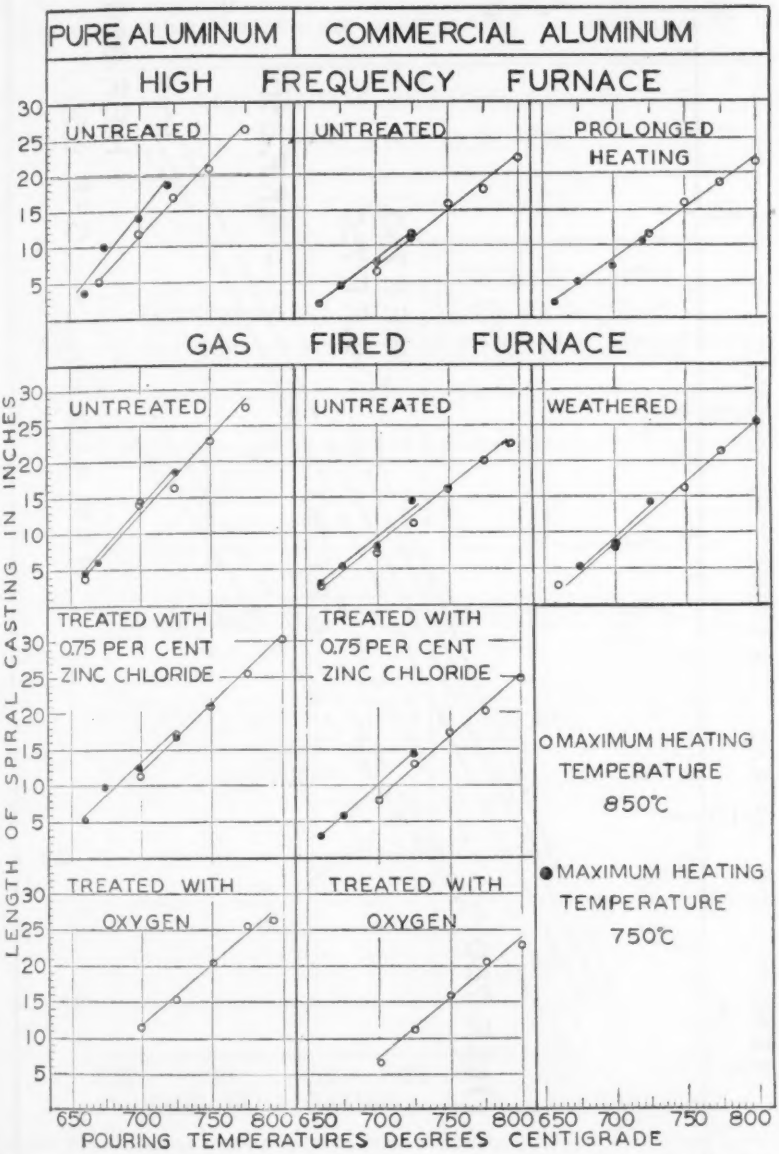

FIGURE 4.—*Running qualities of pure and commercial aluminum, treated and untreated, heated in high-frequency induction and gas-fired furnaces to maximum temperatures of 750 and 850° C.*

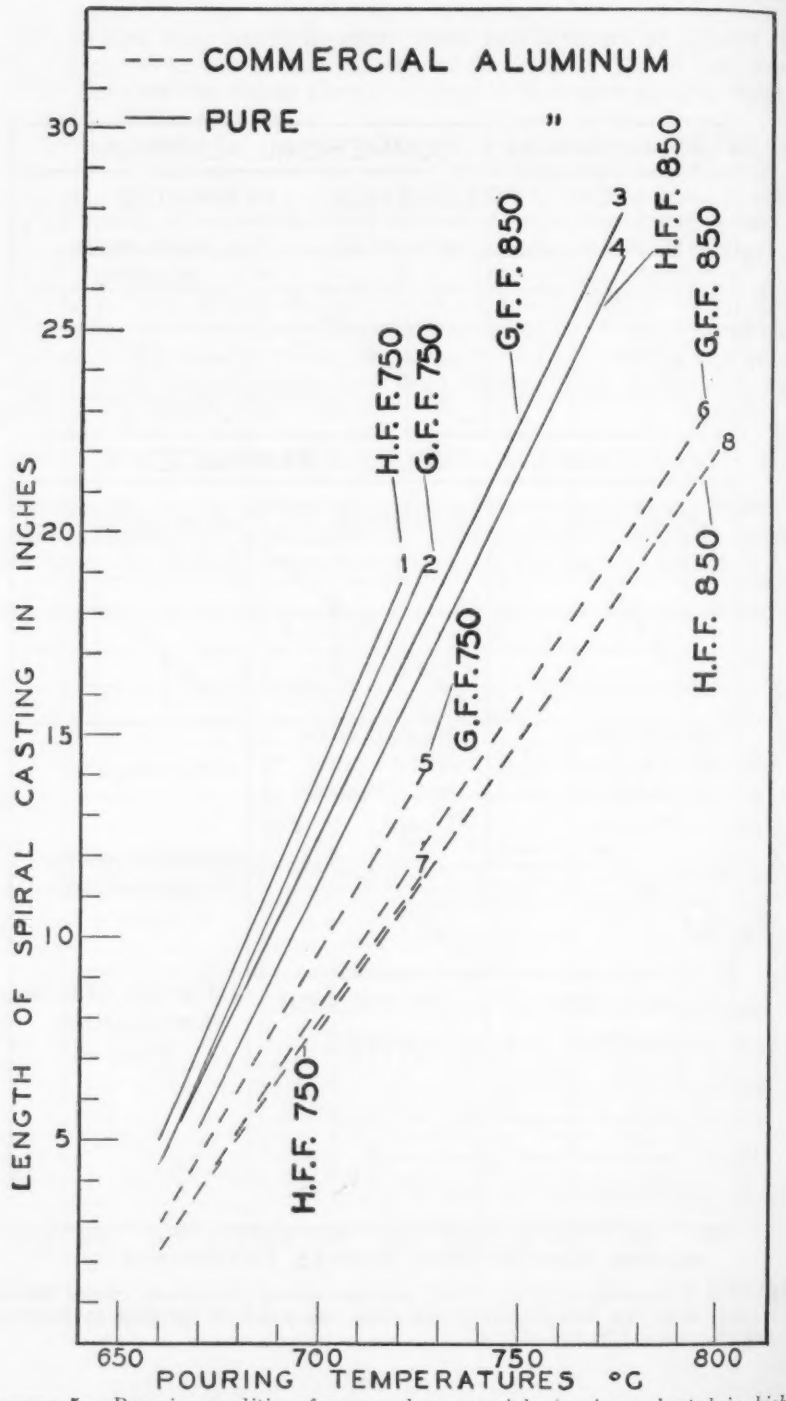

FIGURE 5.—*Running qualities of pure and commercial aluminum heated in high-frequency induction (H.F.F.) and gas-fired (G.F.F.) furnaces to maximum heating temperatures of 750 and 850° C.*

Observations shown in figure 4.

It should be pointed out that the series of points corresponding to any given straight line are observations obtained with a single crucible of metal. Each point represents the pouring of 1 spiral, and successive points represent successive pourings from the same crucible where all conditions, save the pouring temperature, are substantially the

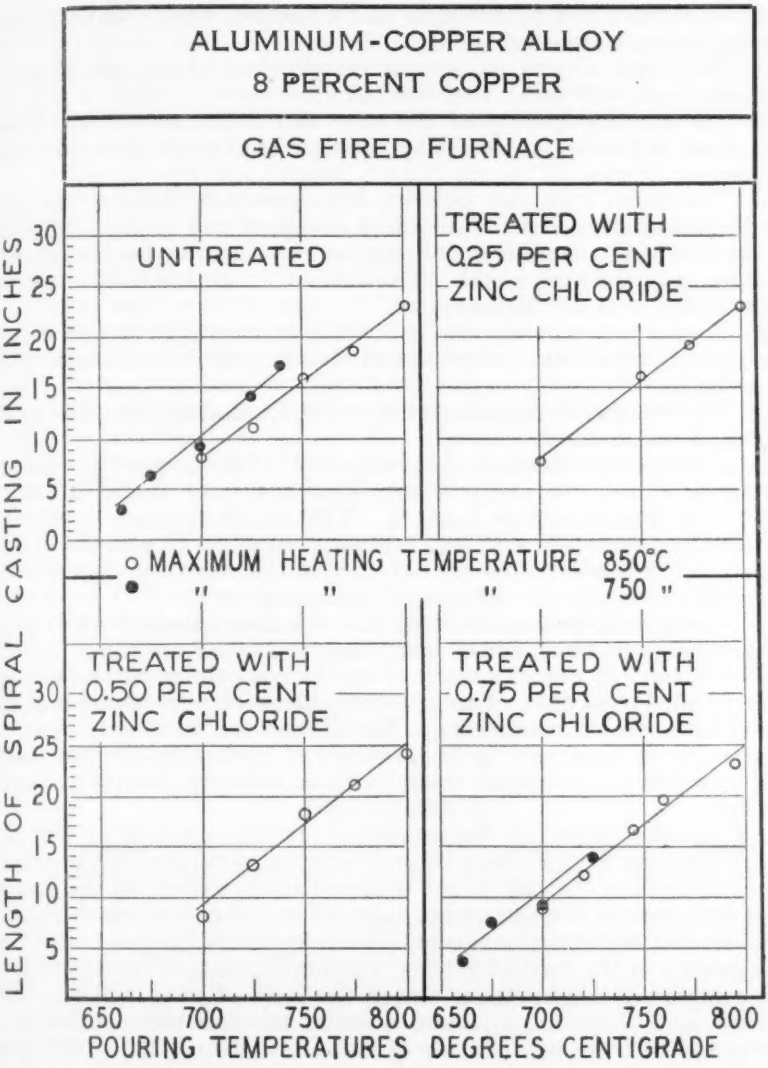

FIGURE 6.—*Running quality of aluminum—8-percent copper alloy melted in gas-fired furnace.*

same. Thus, the points in one such series are probably located relative to each other with far greater precision than could be expected if each point were obtained from a different melt.[2]

[2] A few check heats would have thrown some light on the reproducibility of the slopes of these straight lines, but unfortunately the work had to be discontinued before this was done.

There can be but little doubt that for a given pouring temperature the metals studied have a higher running quality when they have been superheated to 750° C than when they have been superheated to 850° C since no exception to this rule has been found. The magnitude of this effect has not been accurately established but seems, on the average, to correspond to about 10 percent in spiral length.

From table 1 and figures 4, 5, and 6 the following additional conclusions seem warranted:

1. The relation between pouring temperature and length of spirals is linear from 660° to at least 800° C.

2. The running quality of the pure aluminum, regardless of how the metal is treated, is markedly superior to that of the commercial aluminum.

3. Treatment with zinc chloride has apparently little or no effect on the running quality. The effect obtained was slightly beneficial in the case of the commercial aluminum and the alloy but detrimental in the case of the pure metal. The differences are too small, however, to have any real significance.

4. Treatment with oxygen had little or no effect in the case of commercial aluminum but produced shorter spirals in the case of the pure metal.

5. The weathered commercial aluminum behaved the same as the unweathered material.

6. Commercial aluminum heated to 750° C in the gas-fired furnace produced spirals markedly longer than the same metal heated to 750° C in the induction furnace. This single instance is scarcely sufficient to establish with any certainty an effect due to the type of furnace as the observed effects obtained in the other 3 instances where comparison is possible, were small and random.

7. Visual examination disclosed that the metals treated with oxygen contained a great number of both large and small cavities.

The density of castings made of commercial aluminum was invariably greater than that of the castings made of pure aluminum cast under comparable conditions. The differences, however, were evidently due in large part to the presence of cavities in the pure metal and no definite correlations could be found between density and other factors.

All samples taken by the immersed crucible method as well as a number of the stepped bars of pure aluminum formed large internal pipes whereas in the case of the commercial aluminum all the stepped bars and most of the immersion samples were free from such pipes.

The microstructures suggested that porosity in the pure aluminum was mostly in the form of intercrystalline shrinkage crevices while in the commercial aluminum it was in the form of bubble-like cavities.

Saito and Hayashi (2) found a linear relation between length of spiral and pouring temperature of aluminum from 680 to 760° C but obtained the same length of spiral at 880 as at 760° C. Their observations appear to be substantiated in more recent work by Saito and Matsukawa (3) on the viscosity of molten metals measured by means of a rotating cylinder.

The linear relation extending from 660 to 800° C found in the present work does not necessarily contradict the results of Saito and Hayashi, since these authors did not investigate the region between 760 and 880° C. The present results, however, are in exact agree-

ment with those of Courty (4) who finds that the linear relation holds from 658 up to 890° C.

The fact that the spirals obtained with the 8 percent copper alloy were slightly longer than those obtained with the 99.2 percent aliminum is also in agreement with the results of Courty (4) who found that as copper was added to aluminum the lengths of the resulting spirals decreased up to about 2 percent copper content and thereafter increased, the 7 percent alloy yielding about the same spiral length as the 99.3 percent grade of aluminum, and the 8 percent alloy yielding a slightly longer spiral. However the conclusion, which seems to be established, that pure aluminum yields longer spirals than the commercial grade, apparently contradicts the results of Losana (5) who finds a greater fluidity for 98.32 percent aluminum than for 99.26 percent aluminum.

No satisfactory explanation is offered for the decrease in the length of the spirals resulting from superheating to 850° C. Gas absorption by the molten aluminum during melting was suggested in the previous work as a possible explanation of this phenomenon. At the present time it is generally accepted that hydrogen is the gas most readily absorbed by molten aluminum. Methods of removing hydrogen from molten aluminum or aluminum alloys with chlorine, chlorine mixed with nitrogen, or chlorine compounds have been studied by a number of investigators (6,7,8,9,10). The lack of consistent improvement in running qualities from the zinc chloride treatment makes it doubtful that the superheating effect is due to absorption of hydrogen.

According to other investigators (11,12,13) the running quality of aluminum may be affected by the presence of aluminum oxide. Treatment with oxygen produced very little effect except in one case where the treatment resulted in distinctly shorter spirals. This leaves the explanation of the effect on the basis of aluminum oxide formation a probable one.

While no further work is planned at present, it is hoped that opportunity will be offered at some future time to carry this work to a more satisfactory conclusion.

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WASHINGTON, July 21, 1934.

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RESEARCH PAPER RP728

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CRITICAL SOLUTION TEMPERATURES OF SOME HYDROCARBONS IN SULPHUR DIOXIDE[1]

By Robert T. Leslie[2]

ABSTRACT

The variation with composition of the solution temperatures in sulphur dioxide of 17 paraffin and naphthene hydrocarbons of the naphtha fraction of petroleum has been determined. These data have been correlated with the boiling points of the hydrocarbons to determine the possibility of separating nearly constant-boiling mixtures of these hydrocarbons by extraction with sulphur dioxide. A few critical solution temperatures in aniline have been determined to complete a series for comparison with the data for sulphur dioxide. Some experiments on the behavior of the hydrocarbons in ammonia were also made.

It is concluded that sulphur dioxide and ammonia offer little promise as extraction agents to supplement distillation. Aniline shows greater difference than ammonia or sulphur dioxide in its behavior towards 3 classes of hydrocarbons, normal paraffin, iso-paraffin, and naphthene.

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I. INTRODUCTION

The difficulties encountered in the separation by distillation alone of a complex mixture of hydrocarbons, such as that occurring in petroleum can frequently be solved by resort to methods depending upon other physical properties than boiling point. Extraction, which depends on differences in solubilities, is a convenient method and has frequently proved useful, notably for separating nearly constant-boiling mixtures containing olefin and aromatic compounds. It is therefore desirable to obtain information which will aid in predetermining the feasibility of using the process and in selecting the best solvent. To predict the behavior of a distillation fraction on extraction, it would be necessary to determine the phase relations of the solvent and all the constituents, since the hydrocarbons mutually affect one another's solubilities. The critical solution temperatures are, how-

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards representing the American Petroleum Institute.

ever, an easily determinable property on the basis of which qualitative indication of the behavior of hydrocarbons on extraction can be obtained. Since extraction will be of greatest value where compounds which boil close together have considerable differences in critical solution temperatures and since structure has an important influence on the solution temperature, it is to be expected that constant-boiling mixtures containing members of different structural classes (paraffin, naphthene, iso-paraffin, and aromatic compounds) would be more likely to yield to separation by the method than members of a homologous series.

The results presented herein for sulphur dioxide and ammonia are a part of an investigation into the possible use of some extracting agents, boiling at approximately 0° C or below, for the separation of compounds of the naphtha fraction of petroleum. Low-boiling solvents are of particular interest because they can be removed from the hydrocarbon with the minimum amount of manipulation and consequent loss. Since aromatic compounds are known to be extremely soluble in sulphur dioxide, they were not further investigated. Some of the work of other investigators was repeated in order to compare the methods of measurement, but the chief object was to supplement the data which were already available.

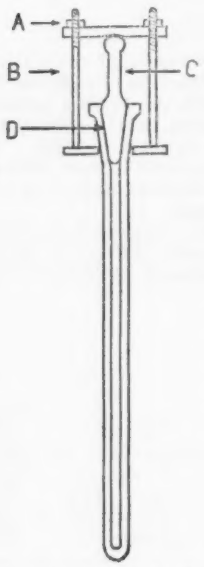

FIGURE 1.—*Tube for observation of solution temperatures.*

A, nuts for clamping tube in frame; B, aluminum frame; C, ground stopper; D, waxed joint.

The values for the critical solution temperatures of the hydrocarbons in aniline were used for reference because the different classes of compounds were known to display considerable differences in solution temperatures in it. Most of these data were available in the literature, but a few were determined in this work to complete the series.

II. METHOD OF STUDY

Weighed amounts of hydrocarbon and solvent were mixed and the solution cooled until the second liquid phase appeared. The stoppered tubes shown in figure 1 were used instead of sealed tubes usually employed. A chlorinated paraffin with a melting point of 70° C, sold as "Opal-wax", was used to seal the stoppers. Care was taken to keep the liquid from coming in contact with the wax. With the stoppered tubes it was possible to obtain a series of points by adding successive quantities of solvent to a given quantity of hydrocarbon. The tubes were of about 3 mm bore and 3 mm wall. This is unnecessarily thick-walled for sulphur dioxide and is sufficient for studies with ammonia.

The experiments with aniline were done in a well-stirred water bath. The temperature at which turbidity was observed, following the first opalescence, was recorded. A mixture of carbon tetrachloride and chloroform cooled with solid carbon dioxide and contained in an unsilvered dewar tube was used for the measurements with sulphur dioxide. The temperatures of separation were much more

definite near the critical points than at lower ones. The bath was cooled rapidly at first to find the approximate solution temperature. It was then reheated and a more careful determination made. No attempt to determine the temperature of disappearance of the 2 liquid phases was made. The points could generally be checked to less than half a degree with different samples but occasional deviations occurred. Most of these were evidently caused by contamination with moisture or other substances, errors in weighing, or nonuniform cooling and the values were discarded.

III. MATERIALS USED

The sources of most of the hydrocarbons are listed in the footnotes to table 1. The journal articles there referred to give methods of preparation and the properties from which the purity can be estimated. None was less than 95 mole percent pure, except for the possible presence of isomers.

The samples of ethylcyclohexane and hexahydromesitylene were supplied by J. D. White and F. W. Rose of this laboratory. Both materials were prepared by the hydrogenation of the corresponding aromatic compounds in acetic acid solution in the presence of platinum black. After hydrogenation, the products were washed with concentrated sulphuric acid and then sodium carbonate solution, and distilled from solid sodium hydroxide. The properties of the ethylbenzene from which ethylcyclohexane was prepared are reported by White and Rose.[3] The hydrogenation product had the following physical constants: n_D^{25} 1.4306; bp 131.6° C, cst in aniline 44° C. The constants reported by Garner and Evans [4] for ethylcyclohexane are n_D^{25} 1.4298; bp 131.6; and cst in aniline 43.8° C. The properties of the mesitylene which was used in the preparation of hexahydromesitylene are reported by Mair and Shicktanz.[5] The hexahydromesitylene had the following constants: n_D^{25} 1.4248; fp −50.7° C, and bp 138.9° C. Properties of cis- and trans-modifications have been reported by Eisenlohr,[6] but it was not determined whether the product used in this work was a pure modification or a mixture.

The hydrocarbons and the aniline were distilled from sodium and kept over the same metal until they were pipetted into the tubes. Sulphur dioxide was condensed from a cylinder of the commercial product and was redistilled into the tubes through a glass capillary.

III. RESULTS

The curves from which the critical solution temperatures in sulphur dioxide were obtained are shown in figures 2, 3, and 4. These curves are probably not as flat as drawn, but the curvature is within the limit of error of the determinations. Only a sufficient part of each of the solubility curves with aniline was determined to fix the critical temperature, and the curves are not reproduced.

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[4] J. Inst. Pet. Techn. **18**,751(1932).
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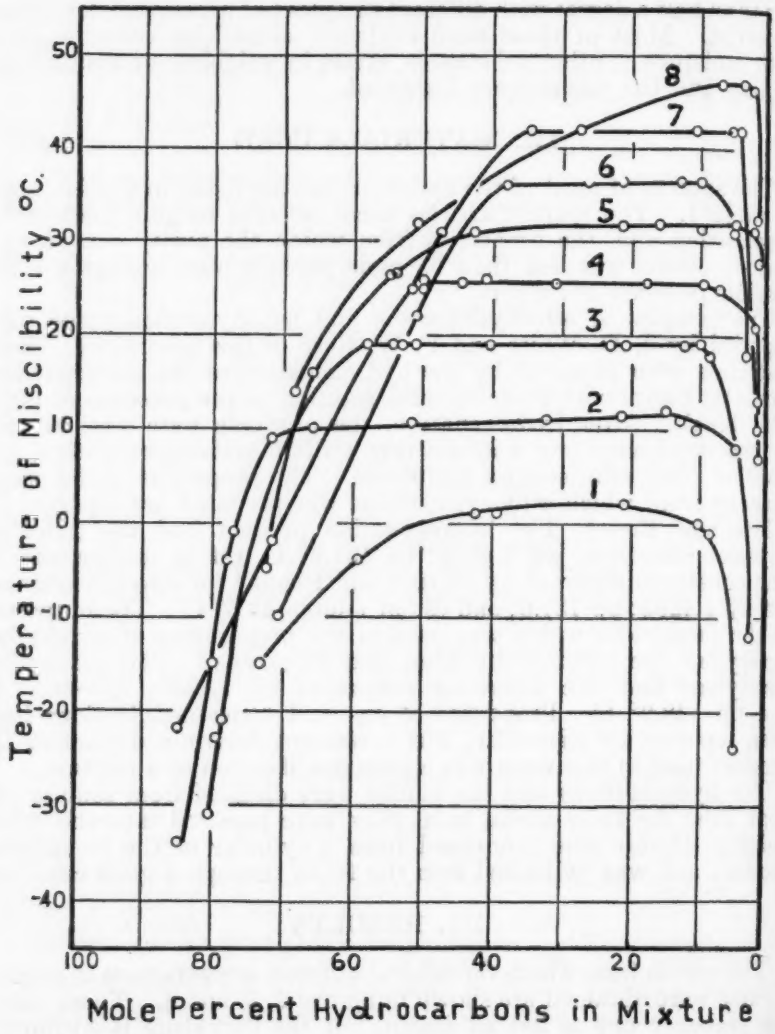

FIGURE 2.—*Solution temperature curves of normal hydrocarbons in sulphur dioxide.*

1. Pentane
2. Hexane
3. Heptane
4. Octane
5. Nonane
6. Decane
7. Undecane
8. Dodecane

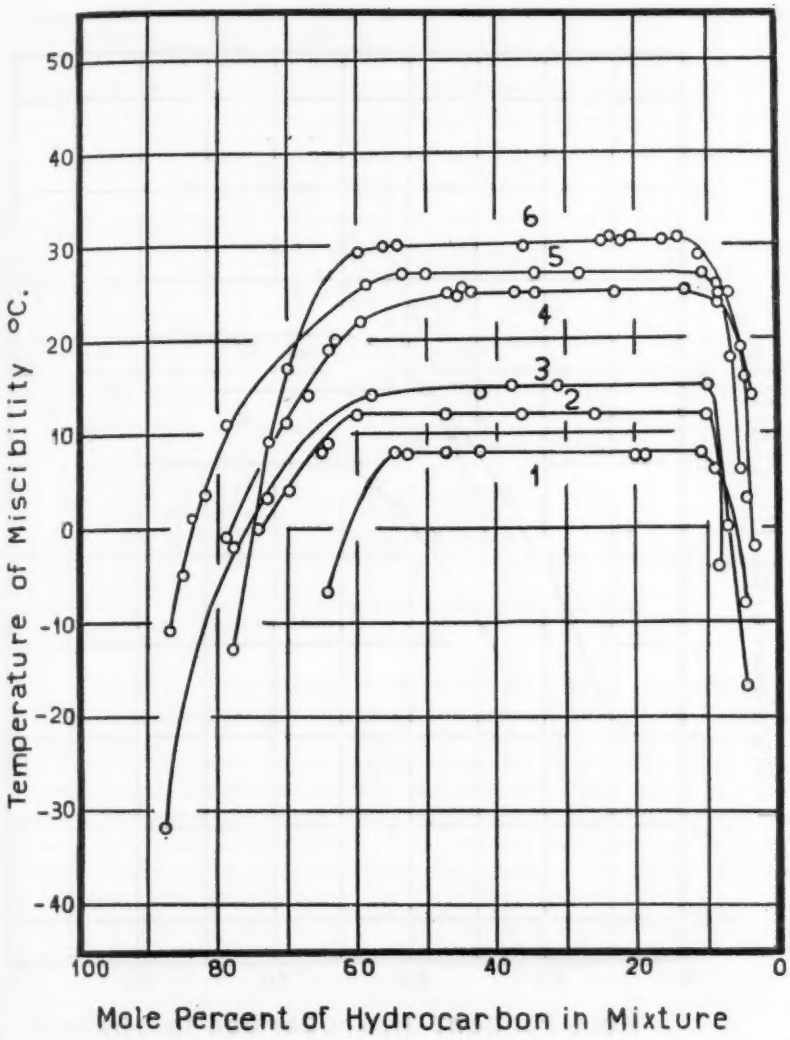

FIGURE 3.—*Solution temperature curves of cyclic hydrocarbons in sulphur dioxide.*

1. Methylcyclopentane
2. Cyclohexane
3. Methylcyclohexane
4. Ethylcyclohexane
5. Nonanaphthene
6. Hexahydromesitylene

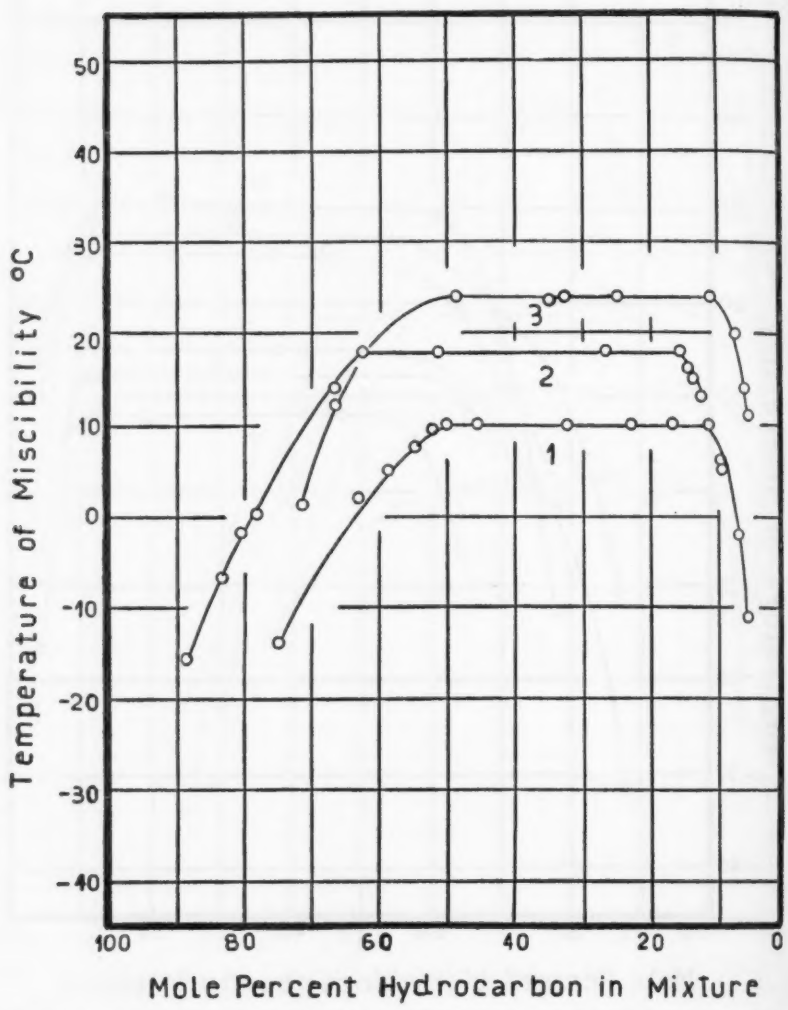

FIGURE 4.—*Solution temperature curves of iso-paraffin hydrocarbons in sulphur dioxide.*

1. 2-Methylpentane
2. 2-Methylhexane
3. 2-Methylheptane

The critical solution temperatures in sulphur dioxide are listed in table 1 together with those found by Seyer and Todd.[7] The maximum difference in the results obtained is approximately 2 degrees, which may have been caused by differences in the method and materials used. All the results reported in this work were obtained by one observer, using a uniform procedure.

TABLE 1.—*Critical solution temperatures of hydrocarbons in sulphur dioxide*

Hydrocarbon [a]	cst (This work)	cst (Seyer and Todd)	Hydrocarbon [a]	cst (This work)	cst (Seyer and Todd)
	°C	°C		°C	°C
Butane [1]	-------	−4.7	Ethylcyclohexane [9]	25	-------
Pentane [2]	2	-------	Octane [8]	25.5	26.9
2-Methylpentane [3]	10	-------	Nonanaphthene [10]	27	-------
Hexane [2]	12	10.2	Hexahydromesitylene [9]	30.5	-------
Methylcyclopentane [4]	8	-------	Nonane [11]	32	-------
Cyclohexane [9]	12	-------	Decane [2]	36.5	37.3
2-Methylhexane [6]	18	-------	Undecane [2]	42	-------
Heptane [2]	19	-------	Dodecane [2]	47	47.3
Methylcyclohexane [7]	15	-------	Dotriacontane [1]	-------	110.0
2-Methylheptane [5]	24	-------			

[a] Superior numbers refer to following literature describing properties of hydrocarbons used:
[1] F. Seyer and E. Todd, Ind. Eng. Chem. **23**, 325(1931).
[2] B. J. Mair, BS J.Research, **9**, 457(1932).
[3] J. H. Bruun and M. M. Hicks-Bruun, BS J.Research **5**, 933(1930).
[4] M. M. Hicks-Bruun and J. H. Bruun, BS J.Research **7**, 799(1931).
[5] J. H. Bruun and M. M. Hicks-Bruun, BS J.Research **7**, 607(1931).
[6] J. H. Bruun and M. M. Hicks-Bruun, BS J.Research **10**, 465(1933).
[7] J. Timmermans and F. Martin. For properties see reference M. M. Hicks-Bruun and J. H. Bruun, BS J.Research 8, 536(1932).
[8] R. T. Leslie, BS J.Research **10**, 609(1933).
[9] J. D. White and F. W. Rose. Preparation and properties reported in this paper.
[10] J. D. White and F. W. Rose, BS J.Research.
[11] J. D. White and F. W. Rose, BS J.Research **7**, 907(1931).

The 4 critical temperatures in aniline which were determined in this work were included in figure 5 and are designated by numbers alone without letters. The footnotes to the figure give the sources of the data which were taken from the results of other investigators. A determination for iso-octane was made because the value of 74° C given by Chavanne and Simon [8] was only estimated from observations on iso-hexane and iso-heptane. The critical solution temperature in aniline of the same material which was used in the work with sulphur dioxide was found to be 75° C. The values of 56.9° C for hexahydromesitylene and of 57° C for the nonanaphthene have not previously been reported. The cst of ethylcyclohexane was determined to compare it with that found by Garner and Evans,[9] since insufficient material was at hand to establish its purity by determining its freezing point.

IV. DISCUSSION

In figure 5 the data on critical solution temperatures have been correlated with the boiling points to show the possibilities of supplementing distillation by extraction. For the normal and iso-hydrocarbons from hexane to tetradecane the relation is nearly linear. Seyer and Todd [10] plotted the relationships between molecular weight and critical solution temperatures for some hydrocarbons, from bu-

[7] Ind. Eng. Chem. **23**, 325(1931).
[8] Compt. rend. **168**, 1111(1919).
[9] See footnote 4.
[10] See footnote 7.

tane to dotriacontane, against the molecular weight and obtained a smooth curve.

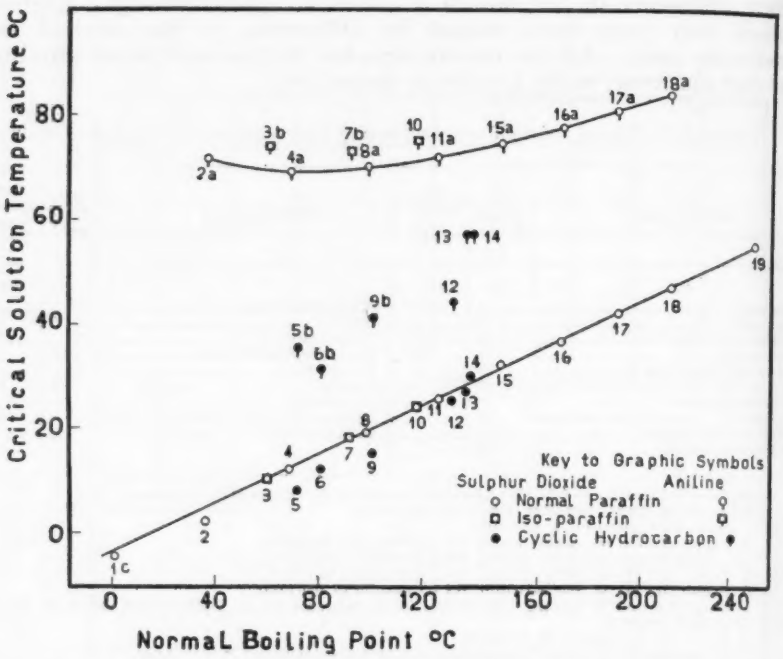

FIGURE 5.—*Relation of critical solution temperature of some hydrocarbons in sulphur dioxide and aniline to the normal boiling points*

1. Butane.
2. Pentane.
3. 2-Methylpentane.
4. Hexane.
5. Methylcyclopentane.
6. Cyclohexane.
7. 2-Methylhexane.
8. Heptane.
9. Methylcyclohexane.
10. 2-Methylheptane.
11. Octane.
12. Ethylcyclohexane.
13. Nonanaphthene.
14. Hexahydromesitylene.
15. Nonane.
16. Decane.
17. Undecane.
18. Dodecane.
19. Tetradecane.

Letters following numbers refer to sources of information taken from other investigators as follows:
a. A. F. Shepard, A. L. Henne and T. Midgley, J. Am. Chem. Soc. **53**, 1948(1931).
b. C. Chavanne and L. J. Simon, Compt. rend. **168**, 1111(1919).
c. W. F. Seyer and E. Todd, Ind. Eng. Chem. **23**, 325(1931).

The critical solution temperatures in sulphur dioxide of all the cyclic hydrocarbons which were examined, with the exception of hexahydromesitylene, fell below the boiling point-critical solution temperature line of the paraffin and iso-paraffins but there appears to be no marked regularity. The lack of regularities of the values may be the result of different influences of ring and side-chain structures.

The critical solution temperatures in aniline are plotted in figure 5 for comparison with the values in sulphur dioxide. There is a uniformity in the relationship for paraffin and iso-paraffin hydrocarbons, but the cyclic compounds again display irregularities. It is apparent that there is a much greater difference in the solution temperature of paraffin, iso-paraffin and naphthene hydrocarbons in aniline than in sulphur dioxide.

A cursory investigation with ammonia, using about equal volumes of hydrocarbon and solvent, indicated that the solution temperatures for normal and iso-paraffins from hexane to dodecane vary more or less linearly with the boiling points between 60 and 80° C. The cyclics lie, in general, a few degrees below the normal compounds, while ethylbenzene, *o*-, *m*-, and *p*-xylene become completely miscible in the neighborhood of 15° C.

V. CONCLUSIONS

The slight differences in critical solution temperatures offer little promise for the use of extraction with sulphur dioxide and probably ammonia to separate paraffin, iso-paraffin, and naphthene hydrocarbons in the naphtha faction of petroleum whose boiling points lie close together. Aniline appears to be more promising for the purpose than sulphur dioxide and ammonia.

WASHINGTON, August 14, 1934.

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